Russian Chemical Reviews **77** (2) 105 – 135 (2008) © 2008 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2008v077n02ABEH003709

Mechanochemical synthesis of complex oxides

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Contents

I.	Introduction	105
II.	Devices for carrying out mechanochemical synthesis	107
III.	The mechanism of ultrafast mechanochemical synthesis: general information	110
IV.	Comparing mechanisms of ultrafast mechanochemical synthesis in AGO-2 impact mills and in 'Fritsch' ball mills	115
V.	Structural types of complex oxides prepared by mechanochemical synthesis	116
VI.	Conclusion	131

Abstract. Devices used to carry out mechanochemical transformations are described. General information on the threshold mechanism of ultrafast mechanochemical synthesis in oxide systems (oxide melting points up to 3000 K) in high-energy mills are presented. Results of structural studies of complex oxides prepared by mechanochemical synthesis are analysed. Specific structural features of metastable complex oxides including high structure disorder, high vacancy concentration and inhomogeneous chemical composition are distinguished. These features are responsible for the unusual properties of mechanochemically produced nanopowders. It is noted that currently mechanochemical synthesis is becoming a competitive method for preparation of oxides and nanomaterials. The bibliography includes 277 references.

I. Introduction

Mechanochemistry studies chemical and physicochemical processes that are either stimulated by mechanical treatment of solids or change their rates as a result of mechanical pretreatment. The most widely known monographs and reviews [1–17] provide detailed reports on the state-of-the-art in mechanochemistry with emphasis placed on those fields of research where the authors work. In particular, Heinike [1] mainly considered chemical and physicochemical processes that occur on friction and fracture and involve the formation of the active surface of solids and reactions between solids and the gas and liquid phases. In his monograph Avvakumov [2] treated mechanical activation of chemical processes, *i.e.*, changes in the reactivities of solid substances as a result of intense mechanical treatment (mainly in planetary mills). Monographs [3–7] are devoted to processing of mineral raw materials using mechanical activation. Butyagin [8] analysed interrelations between structural disordering of solids under development of a deformation and the reactivity of the solids. Objects considered included polymers, quartz, alkali metal halides and simple oxides MgO, GeO_2 and SnO_2. Whereas most monographs published in the early stage of development of mechanochemistry were devoted to fracture or modification of solids, a book [9] covers all avenues of research in the field of mechanichemical synthesis. Researchers from the USA mainly associated mechanochemistry [10] with mechanical alloying in metallic systems because most studies published in the 1980 – 1990s were carried out in this field. This can first of all be due to great prospects for investigation of metallic systems offered by modern electron microscopy methods.

Usually, mechanical treatment is carried out to accelerate physicochemical processes. Gutman [11] posed an inverse problem, that is, how to reduce metal corrosion using mechanochemical processes. A review [12] analyses various problems and prospects for the development of mechanochemistry from degradation of polymers to explosive synthesis of refractory compounds. Among other emission phenomena, neutron emission upon facture of D-containing crystals was mentioned for the first time. It was pointed out that the results of qualitative observations in mechanochemistry have been accmulated over a period of 100 years; however, no test systems were designed for characterisation of the available devices, which are necessary for comparison of results obtained. A monograph [13] is concerned with the so-called soft mechanochemical synthesis involving the preparation of precursors of complex oxides by intense mechanical mixing of hydroxides or hydrated compounds and salts possessing reduced hardness. Precursors of complex and variable composition in an amorphous or poorly crystallised form undergo transformation to desired oxides with nanosized crystallites under mild annealing conditions after drying and removal of volatile compounds. A brief review by McCormick [14] mainly concerns amorphisation on mechanical treatment.

High dispersion and concentration of unusual defect states should *a priori* lead to manifestation of catalytic activity of materials prepared. Indeed, mechanochemical methods are more widely used in catalysis, especially in recent years.[15,16] In his review Boldyrev [17] considered historical aspects of the development of mechanochemistry and outlined the main

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Received 2 April 2007
Uspekhi Khimii **77** (2) 107 – 137 (2008); translated by A M Raevskiy

avenues of development in this field of scientfic research. In addition to the studies carried out in traditional areas of mechanochemistry he analysed publications on mechanochemical synthesis of solid organic substances, studies on the effect of static pressure and shear pressure on the structures of organic compounds and polymorphic transformations, as well as investigations on modification of organic compounds and pharmaceuticals. Rapid extension of the range of systems under study was pointed out; however, no advances in commercialisation of the results of seemingly promising scientific research were reported. The main reason is the lack of high-performance devices suitable for large-scale production. This is not a problem in the case of synthesis of pharmaceuticals. Based on experience in fracture and modification of solids, one can predict that the preparations will contain trace amounts of impurities due to cleavage of chemical bonds, formation of radicals or activation of reactions with the gas medium. As applied to pharmaceuticals, this type of mechanochemical transformations is obviously undesired. Clearly, research on mechanically stimulated modification of pharmaceuticals has the same goal as investigations of mechanical activation in the case of metal corrosion, that is to understand in order to prevent.

Mechanochemical synthesis of complex oxides and composites (cermets), which are similar in methods of preparation, mass transfer mechanism, morphology, fields of application and methods of investigation, has almost not been considered in the reviews and monographs mentioned above. However, recently a rapid increase in the number of publications concerned with mechanochemical synthesis of complex oxides and cermets has been observed (Fig. 1). This is especially pronounced as compared to a decrease in the number of studies on mechanical alloying. The total number of oxide systems studied approaches a value of 1000. Now there has been an explicit trend of progress of research in this field, which is closely related to the design of nanomaterials. For instance, in the year 1998 (at that time the first version of theory of ultrafast mechanochemical synthesis of complex oxides was developed [18]) mechanochemical transformations were only observed in 40 binary and ternary oxide mixture. Among them, only 50% of experiments gave monophase or almost monophase samples (Table 1). The formation of new phases in Ba–Cu–O,[19] La–Mo–O,[22] V–Mo–O (Ref. 25) and Zn–Mo–O (Ref. 20) systems was observed. This was very important for mechanochemistry of oxides, because provided direct proofs of fundamental difference between the mechanism of mechanochemical synthesis and conventional mechanisms of synthesis involving diffusion of components towards boundaries of crystalline nuclei.

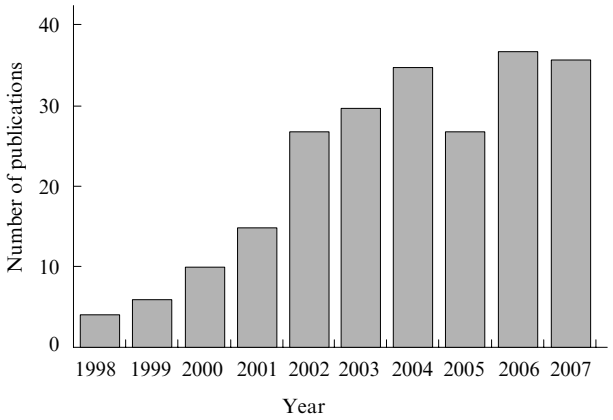


Figure 1. Annual numbers of publications on mechanochemistry of oxides since the year 1998 (data for the first six months of the year 2007 are doubled).

Table 1. Complex oxides prepared by mechanochemical synthesis before the year 1998.

Starting mixture	Product	Structure	Ref.
$PbO + TiO_2$	$PbTiO_3$	perovskite	19, 20
$Pb_3O_4 + 3\,TiO_2$	$PbTiO_3$	"	19, 20
$1.5\,PbO + Nb_2O_5$	$Pb_{1.5}Nb_2O_{6.5}$	pyrochlore	21
$PbO + MoO_3$	$PbMoO_4$	scheelite	19
$Pb_3O_4 + 3\,MoO_3$	$PbMoO_4$	"	19
$PbO + WO_3$	$PbWO_4$	"	19
$Pb_3O_4 + 3\,WO_3$	$PbWO_4$	"	19
$BaO_2 + MoO_3$	$BaMoO_4$	"	19
$BaO_2 + WO_3$	$BaWO_4$	"	19
$SrO_2 + MoO_3$	$SrMoO_4$	"	19
$SrO_2 + WO_3$	$SrWO_4$	"	19
$CaO + MoO_3$	$CaMoO_4$	"	19
$CaO + WO_3$	$CaWO_4$	"	19
$CdO + MoO_3$	$CdMoO_4$	"	19
$CdO + WO_3$	$CdWO_4$		19
$HgO + MoO_3$	$HgMoO_4$		19
$HgO + WO_3$	$HgWO_4$		19
$ZnO + WO_3$	$ZnWO_4$	sanmartinite	19
$MnO + WO_3$	$MnWO_4$	hübnerite	19
$CoO + WO_3$	$CoWO_4$		19
$MgO + WO_3$	$MgWO_4$		19
$La_2O_3 + 2\,MoO_3$	$La_2Mo_2O_9$		22
$La_2O_3 + 2\,MoO_2$	$La_2Mo_2O_7$		22
$La_2O_3 + 2\,MoO_3$	$La_2Mo_2O_{8.5-x}$	new phase	22
$NiO + Fe_2O_3$	$NiFe_2O_4$	spinel	23
$2\,Sm_2O_3 + 3\,Bi_2O_3$	$Sm_{0.4}Bi_{0.6}O_{1.5}$	fluorite	24
$CeO_2 + 4\,Sm_2O_3$	$Ce_{0.2}Sm_{0.8}O_{1.6}$	"	24
$7\,CeO_2 + 1.5\,Bi_2O_3$	$Ce_{0.7}Bi_{0.3}O_{1.85}$	"	24
$2\,Y_2O_3 + 3\,Bi_2O_3$	$Y_{0.4}Bi_{0.6}O_{1.5}$	"	24
$Y_2O_3 + Sm_2O_3 + 3\,Bi_2O_3$	$Y_{0.2}Sm_{0.2}Bi_{0.6}O_{1.5}$	"	24

Mention should be made of the first mechanochemical synthesis of a new compound by the reaction [19]

$$2\,BaO_2 + Cu_2O \longrightarrow BaCuO_x\,.$$

The monoclinic $BaCuO_x$ phase was ascribed a perovskite-like structural motif, according to which peroxide ions cause the B positions to be half-filled in a staggered fashion: $(Ba_6Cu^+Cu^{2+})Cu_4^{2+}O_{9.5}(O_2^{2-})_2$ (Refs 20 and 26). The formation of this metastable phase was observed only after prolonged (30 min), very intense treatment of a $BaO_2 + CuO$ mixture in an AGO-2 mill [centrifugal factor $g = 60$; balls made of tungsten carbide in cobalt matrix (WC/Co cermet, or pobedit] and under explosive synthesis at a theoretical adiabatic temperature of 900 °C. The yield of the $BaCuO_x$ phase in the latter case was at most 15%, being as high as about 80% after mechanochemical synthesis in the AGO-2 mill. An attempt [26] to reproduce the synthesis of this phase using steel balls (steel has a halved density compared to pobedit) led to a compound that is structurally similar to a known cubic phase $BaCuO_2$ with the unit cell parameter $a = 18.58(2)$ Å (PDF 38-1402,† $a = 18.2855$ Å); the greatest value for the

† Hereafter listed are the data retrieved from the Joint Committee on Powder Diffraction Standards (JCPDS) diffraction database.

phases prepared by mechanochemical synthesis. A $La_2Mo_2O_{8.5-x}$ phase was also prepared by mechanochemical synthesis by treating a $La_2O_3 + 2\,MoO_3$ mixture with WC/Co balls;[22] the phase showed a rather good X-ray diffraction pattern, which made it possible to carry out structural studies. However, the structure of the new phase was not reported probably due to some structural features of the phases prepared by mechanochemical synthesis. In all the systems mentioned above the new phases formed as a result of reduction of the oxides upon prolonged mechanical treatment. The EPR spectra of a sample of the new phase prepared from a $V_2O_5 + 2\,MoO_3$ mixture revealed a high content of V^{4+} (see Ref. 25). It is noteworthy that the structures expected from the mixture stoichiometry considerations were formed irrespective of oxygen excess or deficiency; this is unusual for crystal chemistry which studies dense crystals (see Table 1). The unit cell parameters of the phases prepared by mechanochemical synthesis were noticeably different from those of the known phases of the same composition.

Complex oxides are mainly used in production of various ceramic materials, catalysts, fillers, as well as electrode and other materials. An environmentally friendly mechanochemical method of preparation of nanocrystalline or nanostructured oxide materials is in excellent agreement with modern trends in the development of materials science. The lack of high-performance devices on the market presents no problems in the field. For instance, planetary mills with horizontal axis of rotation (*e.g.*, M-3 mill designed by Golosov and PM-1 mill designed by the author of this review) are characterised by a reasonably high performance of about 1 kg h^{-1}, make it possible to prepare high-quality nanopowders and can provide large-scale production after corresponding modification.[27] Correctly chosen systems and appropriately modified models of attritor mills produced by 'Zoz Gmbh' [28] can also be used to this end.

Analysis of literature in the field of mechanochemical synthesis of complex oxides revealed the following.

1. A dramatic increase in the number of oxide systems studied and publications in this field began abroad at the end of the 20th century. This is due to the fact that at that time the materials science laboratories were equipped with high-energy planetary mills that permit significant acceleration of miling process. For systems including heavy-element oxides, a simple increase in the milling duration to tens and hundreds of hours leads to occurrence of mechanochemical synthesis, *i.e.*, formation of target products with no annealing. Researchers from France, Singapore, Japan, PR China, Slovenia, Spain, Canada, Serbia, Brazil, Argentina, Mexico and other countries almost simultaneously and independently employed this feature for preparation of ceramic powders.

2. In Russian Federation a rapid increase in the number of oxide systems studied is to some extent due to the possibility of performing controllable mechanochemical synthesis based on theory of ultrafast mechanochemical synthesis of complex oxides [18,29] and to the use of high-energy mills (most of them were designed at research institutes belonging to the Siberian Branch of the Russian Academy of Sciences) that allow the duration of mechanochemical synthesis to be shortened by an order of magnitude and more compared to the duration of process carried out using conventional laboratory mills made abroad.

3. The lack of unified and self-consistent terminology strongly hampers the search for relevant studies using key words and prevents the progress in this field of science. This situation lasts since the early stages of development of mechanochemical synthesis and cannot be improved as yet. For instance, mechanochemical synthesis of complex oxides is called reactive millig, mechanochemical activation, mechanical alloying, high-energy ball milling, mechanochemical grinding, *etc*. At the same time often preliminary grinding of oxide or other reactant mixtures in high-energy mills followed by annealing to perform a solid-phase synthesis is unreasonably called mechanochemical synthesis [30] or soft mechanochemical synthesis.[13]

4. Many researchers use the milling duration as the most important (often, as the one and only) parameter characterising the powder treatment procedure. But the mechanical treatment procedure is often not described. This excludes the possibility of quantitative comparison of results obtained.[8] Often, different researchers study identical systems but obtain opposite results, which cannot be explained. Qualitative observations have been accumulated so far. No parameters for characterisation of the quality of powders prepared are available, although it is obvious that contamination is unavoidable. Materials prepared by mechanochemical synthesis are by default thought to have the same compositions as the starting oxide mixtures; this may lead to significant errors.

5. The 'new generation' of materials scientists who revealed mechanochemical effects in experiments carried out with modern laboratory mills are not familiar with the previously published studies in the field of mechanochemistry. In a large number of studies references to earlier publications are formal, fragmentary of absent at all.‡

6. Almost without exception the mechanochemical method is used for green synthesis of known materials as an alternative to traditional techniques. There are almost no studies on quantitative relations between mechanical loading and chemical response, which would serve as a basis for elucidation of the mechanism of the process and thus develop a controllable synthetic procedure. At the same time almost all publications include speculations on a possible mechanism of the process or the need of carrying out corresponding investigations.

Numerous observations of mechanochemical synthesis of complex oxides should not deceive researchers that a routine method of synthesis of all oxide compounds has been developed. There is a large number of systems in which mechanochemical synthesis does not occur.[19] To understand the processes of mechanochemical synthesis and subsequent target preparation of complex oxides, one should answer the question why does mechanochemical synthesis occur selectively? Since there is lack of designated journals information on mechanochemical synthesis of complex oxides has been almost randomly published in a variety of scientific journals, most of which cover the materials science problems. In addition, no reviews on mechanochemistry of oxides (this avenue of research shows the most dynamic progress and offers great prospects for practical applications) have been reported as yet. The aim of this review was to bridge the gap.

II. Devices for carrying out mechanochemical synthesis

Most studies on mechanochemistry of oxides were carried out using planetary mills with vertical axis of rotation, *e.g.*, the AGO-2 mills [33] (Fig. 2), various models of the Fritsch, Retsch

‡ Examples are provided by the title 'First Direct Synthesis By High Energy Ball Milling ...' (Ref. 22) and fragments of abstracts from some articles: '... novel mechanochemical activation route ...' (Ref. 31), '... first mechanochemical synthesis of nanosized perovskite powders ...', *etc*.[32]

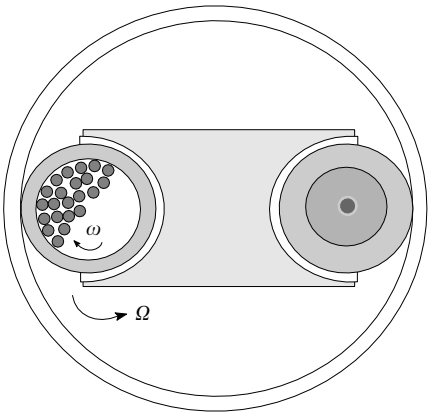


Figure 2. Scheme of AGO-2 planetary mill.[33]



Figure 3. General view of PM-1 mill with lined drums, rapid load – unload options and independent rotation of drums and disk.

and SPEX mills, as well as home-made planetary mills. This type of mills is characterised by two main parameters, the rate of drum rotation about its axis ω and the disk rotation rate Ω. New models of the 'Fritsch' mills (Vario-Planetary Mill Pulverizette 4) allow these parameters to be varied independently. This feature was provided in the PM-1 mill designed two decades ago (Fig. 3). By varying the ω-to-Ω ratio and some other less important parameters it is possible to implement different regimes of the motion of the balls, from the so-called attrition (especially at a large number of balls) to shock loading.[2, 10, 34] If the number of balls is small, as in the most widely used 'Fritsch' mills, the main method of loading the powder is rolling.

Comparison of different mills is a highly complicated task. Indeed, one should allow for a variety of parameters, but there is lack of commonly recognised test systems (design of such systems in turn requires understanding of the mechanism of mechanochemical transformations). Taking different processes as examples, this problem was elucidated by many researchers including Kolosov,[35] Abdellaoui and Gaffet [36–38] (mechanical alloying), Murty *et al.*[39] (amorphisation of alloys), Rojac *et al.*[40] (mechanochemical synthesis of complex oxides), Delogu *et al.*,[41–43] Zyryanov (mechanical activation of MgO [44] and grinding of $BaTiO_3$) [27, 45] and Kaminsky and Musatov.[46] The efficiency of grinding in the most high-energy mills operating in the shock regime and having similar parameters is compared in Table 2 taking a classical model system, barium titanate, as an example.

The parameters of the powders treated in the mills with horizontal axis of rotation are much better than those of the powders treated in the AGO-2 mill with vertical axis of rotation. However, the M-3 and PM-1 mills are almost not used for mechanochemical studies, because one should have about 0.1 kg of powder per drum only for lining the steel balls and nearly the same amount of powder for treatment under optimum conditions. Planetary mills with horizontal axis of rotation are much more complicated in design. They are somewhat different from conventional vertical mills in mode of the motion of steel balls. By optimising parameters of the devices it is possible to increase the proportion of high-energy collisions; in the future this will allow one to design a new generation of activators. Planetary mills are mainly used for preparation of large amounts of materials (batches). They provide good examples for considering the prospects for mechanochemical technology in fabrication of nanomaterials.

An AGO-2 universal laboratory mill has a simple design and allows the rotation rate to be varied (g-factor is varied in stepwise fashion, namely, 20 – 40 – 60). The possibility of varying the composition of the atmosphere in and the temperature of hermetically closed drums extends the range of systems to be (potentially) treated; the drum volume seems to be optimum for carrying out experimental research. The mill has many drawbacks; to some extent this is a result of simplicity and versatility of the device. A friction drive does not provide reliable reproducibility of treatment. Powders thus prepared are inhomogeneous, show a high degree of aggregation and therefore cannot be used for preparation of dense ceramic

Table 2. Characteristics of $BaTiO_3$ powders.[27]

Mill model	Axis of rotation	Cooling	Volume [a] /litre	Fe impurity (mass %)		Specific surface area /$m^2\ g^{-1}$	Performance /$kg\ h^{-1}$
				conventional continuous treatment	correct treatment		
M-3 (Ref. 47)	horizontal	air	2.0 × 0.6	0.3 – 0.5 [b]	0.004 – 0.008 [b]	22 ± 3 [b]	0.4 [b]
				0.15 – 0.3 [c]	0.002 – 0.005 [c]	13 ± 2 [c]	0.8 [c]
PM-1 (Ref. 48)	"	"	4.0 × 0.75	0.2 – 0.4 [b]	0.003 – 0.005 [b]	13 ± 2 [b]	1.0 [b]
				0.1 – 0.2 [c]	0.001 – 0.003 [c]	9 ± 2 [c]	2.0 [c]
AGO-2 (Ref. 33)	verical	water	2.0 × 0.15	0.5 – 1.0 [b]	0.05 – 0.10 [b]	9 ± 2 [b]	0.02 [b]
				0.3 – 0.5 [c]	0.02 – 0.04 [c]	6 ± 2 [c]	0.04 [c]

Note. The initial specific surface area of the powder is 1 $m^2\ g^{-1}$; grinding duration was 360 s; steel balls 9 mm in diameter; centrifugal factor $g \approx 60$.
[a] The first and second figures denote the number of drums and the drum volume, respectively. [b] At a ball mass to material mass ratio of 20. [c] At a ball mass to material mass ratio of 10.

materials without additional purification, separation and disaggregation.[19]

When using steel balls (especially in the AGO-2 high-energy mills with vertical axis of rotation), it is of great importance to follow a correct procedure[49] for mechanical treatment of powders. The procedure involves preliminary preparation of the working surface, coating of the surface with the material or composition to be processed and meeting such mechanical treatment conditions under which the coating is retained. Usually, the balls-to-material charge ratio is at most 20 by mass and the duration of continuous treatment is 30–60 s (100–200 s for mills with horizontal axis of rotation); then, the mill is stopped and the charge in the drum is mixed. This allows the material to be unloaded from the dead zones of the drum, which retains the drum lining and provides a minimum contamination and macroscopic homogeneity of the powders. When doing a research and in order to retain metastable states, it is important to perform mechanical treatment at nearly constant temperature of the ball charge, about 300 K. When a mill operates in a conventional regime (continuous action), the temperature of the balls can be as high as $\sim$850 K.[50]

Grinding of powders unavoidably causes contamination. Materials for balls and drums should possess high wear resistance. In this respect a WC/Co cermet as well as zirconia and corundum ceramics are the best.[10] However, brittle ceramic balls and even WC/Co balls fail under shock operation of planetary mills; because of this, the energy intensity of the devices is reduced and shock operation is avoided. In addition, ceramic balls, especially those made of alumina ceramics, have a low density and therefore mechanochemical transformations are only possible on prolonged treatment and the range of appropriate systems is very limited. Recently, balls based on HfO_2 ceramics (ball density is 10 g cm^{-3}, which is higher than the density of steel) have been available on the market; however, the mills equipped with such balls are costly. It seems that an optimal system for high-energy ball milling of powders [especially with allowance for the possibility of additional processing of aggregated nanopowders using electromass-classifier (EMC) technique[51,52]] includes a planetary mill characterised by $g \approx 60$ (impact velocity lower than $\sim$10 m s^{-1}, because even steel balls break down at higher impact velocities), having a horizontal axis of rotation and equipped with steel balls provided the use of the correct procedure for mechanical treatment[49] and(or) its modifications. The method for preparation of high-quality nanopowders using a combination of the PM-1 and EMC devices and the correct procedure for mechanical treatment was called mechanochemical ceramic technology.[19,20,53]

Considerable literature on the dynamics of balls in planetary mills is available (see, *e.g.*, Refs 2, 10, 34, 36, 37, 54–58). However, the motion of balls is described using many approximations; the same holds for calculations of collision energy distribution. Various kinds of supply of mechanical energy to the substance are reduced to shock action. The collision energy distribution can hardly be used for comparing with the chemical response. Therefore, the notion 'average impact' was introduced.[18,20,29,40] The impact energy is the most important parameter characterising the mechanochemical effect.[36,37,40–43] For instance, based on the results of a study,[31] it was shown[40] that mechanochemical synthesis of $SrTiO_3$ requires a minimum impact energy; indeed, the process does occur at an energy of 185 mJ and does not occur at 50 mJ and lower energies. However, the average impact energy in the AGO-2 mill (g = 60; steel balls 10 mm in diameter) is only 30 mJ and the half-conversion time of most systems studied[19] is of the order of 10^2 s. For comparison: mechanochemical synthesis of $SrTiO_3$ in a Fritsch Pulverizette 6 mill was observed[31] (traces of product were detected) only after 70 h of mill operation! The distinctions are so great that some admissions in the models seem to be incorrect.

The authors of the earlier studies tried to reveal a particular parameter of loading, which would play the key role for mechanochemical transformations. To this end, they studied how the mill parameters (rotation rate, load, ball diameter) affect the physicochemical response using the same sample. However, no considerable advances were made. In their model Burgio *et al.*[59] introduced the notion 'cumulative impact energy normalised to the mass of material' (m),

$$E_{\mathrm{cum}} = \frac{\Delta E v t}{m},$$

where ΔE is the impact energy, v is the impact frequency and t is the treatment duration. It was shown (see, *e.g.*, Ref. 40) that this parameter can be used as a 'yes/no' criterion for mechanochemical synthesis. However, back in 1983 Lyakhov and Boldyrev formulated a requirement, according to which this parameter should be intensive.[60] The expression for cumulative energy does not include parameters of materials.

Other authors who studied the loading–response relationships (metallic systems were mainly investigated) also considered the parameter of loading separately, ignoring its relation to the parameters of the chemical system.[59,61–65] This means that mechanochemical synthesis is totally governed by the device rather than chemical system. However, the results obtained in the experiments with oxide systems[19] showed that parameters of chemical systems should not be ignored. In other words, comprehensive studies of devices for carrying out mechanochemical synthesis and simulation of their operation are useful for optimisation of operating conditions, but are useless for understanding the mechanism of mechanochemical transformations. The plots of loading *vs.* time for different mills are shown in Fig. 4. The loading normalised to the mass

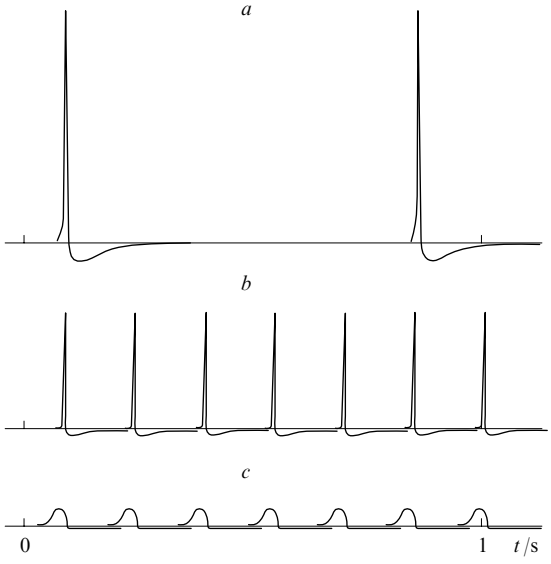


Figure 4. Plots of loading *vs.* time at equal energy supplied for AGO-2 impact planetary mills (*a*), high-frequency vibratory mills (*b*) and rolling-type Fritsch planetary mills (*c*).

of material is determined by the parameters of the device (ball velocity and energy that can be varied by varying the ball diameter and density). Relaxation of energy supplied is determined by the nature of the system under study; therefore, the criterion for occurrence of mechanochemical synthesis should include certain parameters of the system. However, this is ignored in the available publications. If the loading velocity is too low (at the same impact energy), the energy supplied has sufficient time to dissipate and fast mechanochemical synthesis becomes impossible. The average impact velocity for the mills listed in Table 2 is ~ 4 m s^{-1}, which corresponds to an impact loading duration of about 10^{-5} s.

Rolling a ball over a powder layer can also be considered as slow pulsed loading. From geometric considerations one can estimate with ease that at a conventional disk rotation rate of 400 rpm the linear velocity of balls at the wall is ~ 10 m s^{-1}. For a powder layer with a relative density of 0.5 and a thickness of 30 μm the loading velocity of a ball 10 mm in diameter is only ~ 0.15 m s^{-1}. At this loading velocity, almost mechanical energy supplied is dissipated and transformed to heat. Moreover, compaction of powder causes even greater decrease in the loading velocity.

III. The mechanism of ultrafast mechanochemical synthesis: general information

Mechanochemical transformations in chemical systems are mainly studied using devices with multiple and complex-pattern mechanical loading (so-called 'black boxes'). Investigations of the complex mechanism of mechanochemical synthesis are similar to the search for a solution to the 'double black box' problem. The algorithm of solving the problem has been reported in a number of studies.[18, 20, 29]

Quantitative investigations of the 'mechanical loading–chemical response' relationships first of all require knowledge of the relation between the duration of mechanical treatment of a substance in the mill and the energy supplied. Almost all studies *a priori* imply a linear dependence. But this is not the case.[20, 29, 44] Non-linear dependence is particularly pronounced in high-energy planetary mills with vertical axis of rotation (AGO-2, AGO-5, EI, APF, *etc*.). The influence of the procedure for treatment of MgO on the broadening of the EPR lines of Mn^{2+} impurity ions (they are sensitive to mechanical stress in the crystal lattice) is illustrated in Fig. 5. Compaction of powder during mechanical treatment leads to a rapid attainment of saturation, but loosening of the powder and return of material from the dead zone to the active zone (for mills) causes a linear increase in the response to mechanical action.

Thus, the correct procedure for mechanical treatment simultaneously provides (i) reduced contamination of powders by 1 – 3 orders of magnitude; (ii) improvement of macroscopic homogeneity of samples, which is necessary for characterisation by diffraction methods; (iii) temperature of environment of about 300 K; (iv) approximately linear relation between the energy supplied and treatment duration; and (v) improvenent of the efficiency of mechanical treatment.

To study mechanochemical transformations themselves, one should first of all exclude the mechanical 'black box' from consideration. In particular, this was attained [18] by choosing identical conditions for mechanical treatment using the correct procedure and comparison of parameters of the chemical systems with the known parameters in the same-type reactions MO + MoO_3 (WO_3).[19] The half-conversion energy $E_{1/2}$, the average value determined from the consumption of the starting reactants and formation of reaction product (according to powder X-ray diffraction data) was chosen as the parameter of chemical response. This made it possible to eliminate the uncertainty in the notion 'product of a reaction'.

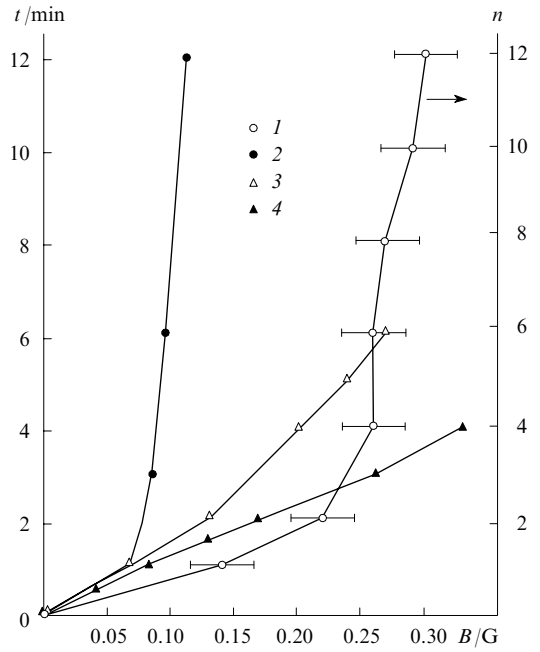


Figure 5. Mn^{2+} impurity EPR line broadening (B) on rolling treatment of MgO on a simulator (*1*), in continuous-action AGO-2 mill (*2*), with mixing after 60 (*3*) and 30 s (*4*);[26, 29]
n is the number of rolling cycles.

Almost all researchers are interested in mechanochemical method as a tool of controlled action on solid substances. In this case to determine the main factors affecting the course of mechanochemical synthesis means to determine its mechanism.[60] To reveal the main factors, it is sufficient to compare various systems. Repeated attempts to estimate the pressures and temperatures developed under shock were made,[2, 66, 67] but no positive results were obtained. Even the problem of the need and possibility of description of a fast and strongly nonequilibrium process in an open system using two thermodynamic parameters, P and T, casts some doubt. A discussion on the thermal and athermal nature of mechanochemical processes began in the 1970 – 1980s (see reviews [1, 2, 8, 12, 17]) but ceased to date.

Analysis of the whole body of experimental data [19] performed during a few years revealed a linear correlation between the mechanical loading and chemical response (correlation coefficient $r = 0.64$). After elimination of the systems characterised by incongruent melting of the expected product in which no mechanochemical synthesis occurred similarly to mechanical alloying in metallic systems the correlation between the mechanochemical yield

$$K = (E_{1/2})^{-1}$$

in units of kg MJ^{-1} and the loading parameter ΔT_z (average heating of the material in the reaction zone due to mechanical energy supplied in the primary loading event) improved to $r = 0.67$ (Fig. 6 *a*).[18, 20] Validity of extrapolation of the kinetic dependences 'mechanochemical yield – energy supplied during the first loading event to a conversion of 0.5 ($\sim 10^1 - 10^2$ events)' was analysed.[18, 20, 29] It was shown that the error introduced in this case is an order of magnitude lower than

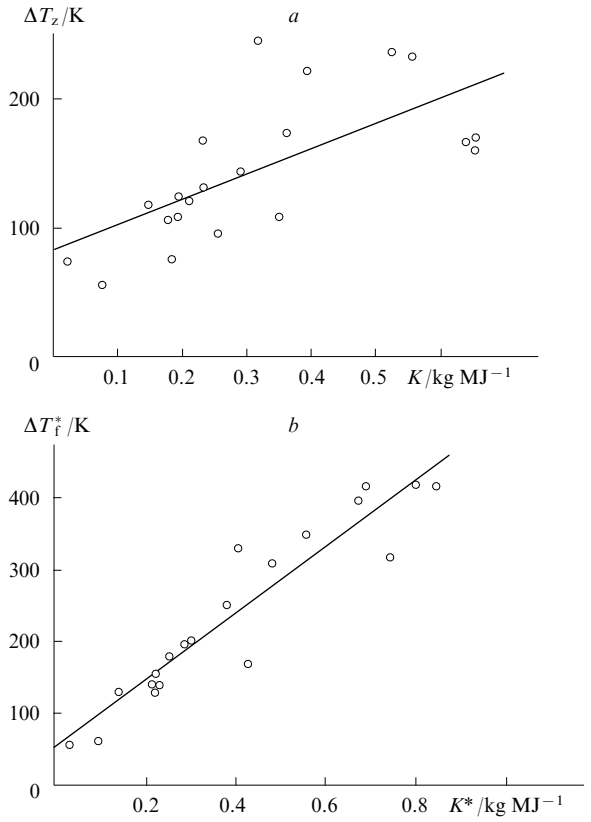


Figure 6. Chemical response plotted *vs.* mechanical loading. $r = 0.67$ (*a*), 0.9437 (*b*). For ΔT_f^* and K^*, see text.

the error in determination of $E_{1/2}$, which is at best $\pm 15\%$. The correlation coefficients obtained upon linearisation in other coordinates were less than 0.47 irrespective of the normalisation of the mechanochemical yield, *e.g.*, 0.47 for $\Delta T_z - (E_{1/2})^{-1}$ with normalisation per mole; less than 0.45 for $\exp(\Delta T_z) - (E_{1/2})^{-1}$ with normalisation per mole or kg MJ^{-1}, *etc*.

The correlation characterised by $r = 0.67$ means that, first, mechanochemical synthesis has a pronounced threshold character (see Fig. 6 *a*: no interaction at a reaction zone temperature below 50 K); second, the mechanical loading parameter ΔT_z includes the properties of the chemical system, that is, the heat capacity, densities of reactants determining the powder volume in the impact zone; and third, the linear dependence on ΔT_z unambiguously shows that mechanochemical synthesis is not due to mass transfer through diffusion. The lack of correlation in the case of normalisation of the mechanochemical yield per mole (as proposed by Butyagin [8]) indicates a non-stoichiometric composition of the product of mechanochemical synthesis. All mechanically assisted processes in the solids have essentially threshold character, but in so great explicit form the threshold character of mechanochemical synthesis was reported for the first time.[18]

The correlation coefficient of this linear dependence considerably increases (to $r = 0.847$) if the mechanical properties of reactants are included by introducing a small correction for the Mohs' hardness difference between the reactants $(E_{1/2})^{-1}\exp(\gamma \Delta MH)$ (where γ is an empirical parameter), *i.e.*, the maximum mechanochemical yield is reached at equal reactant hardnesses. If the difference between the reactant hardnesses, ΔMH, exceeds a value of 4, no mechanochemical interaction occurs.[18,19] This basically distinguishes mechanochemical synthesis from other methods of synthesis and was experimentally observed in many studies. Experiments showed that combinations of reactants with minimum hardness differences are optimal for mechanochemical synthesis.[68–76] The logarithmic scale of Mohs' relative hardness serves for semi-quantitative characterisation of minerals; it correctly characterised the mechanical properties up to a hardness of 8, even in the light of modern considerations of hardness measurements.[77]

Correction of the ΔT_z value for the enthalpy of reaction and the inclusion of energy dissipation improves the linear correlation between the normalised mechanochemical yield

$$K^* = (E_{1/2})^{-1}\exp(\gamma \Delta MH)$$

and the effective temperature, ΔT^*, of the reaction zone and now one gets $r = 0.938$. Phonon-assisted energy dissipation relative to the $HgO + MoO_3$ sample (see §) with similar reactant hardnesses ($\Delta MH = 0.5$) and the internal character of the heat of the chemical reaction was included by introducing the effective temperature of the reaction zone [29]

$$\Delta T^* = \left(\Delta T_z + \beta \alpha_z \Delta T_{ch}\right) \frac{M}{\hat{M}} + \beta \alpha_z \Delta T_{ch} ,$$

where β is an empirical parameter; α_z is the extent of reaction completion after the first loading event (calculated using the average impact energy, energy supplied ($E_{1/2}$) and the parameters that characterise the experimental conditions, namely, the mass of material charge, ball size, drum size, *etc*.[18,20,29]); and ΔT_{ch} is the contribution of the chemical reaction to 'heating'. A simple expression $M/\hat{M}$ ($\hat{M}$ is the molecular mass of the probe, the reference system $HgO + MoO_3$) replaces the modified Debye equation for the phonon contribution to thermal conductivity, which is the main mechanism of heat transfer for dielectrics [78]

$$\lambda_{ph} \sim \frac{T_m^{3/2} \rho^{2/3}}{M^{2/3} T} .$$

where T_m is the melting point, ρ is the density and M is the molecular mass.

The inclusion of non-stoichiometric composition of the product by introducing small corrections to the thermal effect of the reaction and heat dissipation, which do not exceed the errors in experimental determination of $E_{1/2}$, made it possible to improve the linear correlation between the mechanical loading and chemical response to $r = 0.944$ and emphasised the threshold character of the phenomenon (see Fig. 6 *b*). The final form of the equation for the effective temperature is as follows:

$$\Delta T_f^* = [\Delta T_z + \beta \alpha_z \Delta T_{ch} \exp(-\gamma \Delta MH)] \times$$

$$\times \frac{M}{\hat{M}} (1 + k) + \beta \alpha_z \Delta T_{ch} \exp(-\gamma \Delta MH) ,$$

where

$$k = \frac{\Delta MH (M_B - M_A)}{MH_{max} (M_A + M_B)} ,$$

§ The sample was at the centre.

and M_B and M_A are the molecular masses of the softer and harder reactants, respectively.

Thus, linearisation of the dependence of the chemical response on mechanical loading made it possible to reveal the key factors affecting the dynamics of mechanochemical synthesis. These are the molecular masses of reactants (the higher the molecular mass the higher the mechanochemical yield owing to lower heat capacity and thermal conductivity and to smaller volume of the reaction zone due to high density), the enthalpy of the chemical reaction and the Mohs' hardness difference between reactants. The rate (dynamics) of ultrafast mechanochemical synthesis shows no explicit dependence on the particle size; indeed, despite the fact that dispersions of the starting reactants differed by about three orders of magnitude, a good linear correlation between the mechanical loading and chemical response was observed. This again points to a non-diffusion mechanism of primary mass transfer in the course of ultrafast mechanochemical synthesis of complex oxides. Introduction of the effective temperature as the key parameter of mechanical loading (it simultaneously includes the parameters of the mill and the chemical system and the mechanical treatment conditions) is in fact a kind of a compromise between opposite viewpoints on the mechanochemical synthesis as the process (thermal or athermal).

Mechanochemical processes occurring during the primary loading event are described by the generalised equation [29]

$$A + B \rightleftharpoons (A_{1-\delta}B)^* \longrightarrow A_{1-\delta}B^*, \quad (1)$$

where $(A_{1-\delta}B)^* = (D)^*$ is the so-called dynamic state at loading ('black box' according to Butyagin [8, 12]), which represents an atomic mixture of reactants in the form of growing rollers and voids in the contact region between particles A and B (according to Mohs, they are called the harder and softer reactant, respectively) (Fig. 7). As the contact between the rollers and the surface of the parent phase breaks, mechanoemission of electrons and other species occurs,[29, 79] which eventually leads to reduction of oxides. The atomic composition of (D)* and, therefore, of the primary product is determined by the hardness difference between the reactants. Unloading causes the dynamic state to relax under quenching and decompression; a reaction product can also be formed. Butyagin [8, 12, 79] repeatedly emphasised the need to distinguish between the loading and subsequent relaxation of a solid for understanding the mechanochemical processes.[8, 12, 80] At small size of (D)*, relaxation can occur without formation of a product. The harder reactant is always present in deficiency in the primary product $A_{1-\delta}B^*$ (asterisk denotes the origination from the dynamic state); therefore, in the case of ordering the [AB] structure contains a high concentration of vacancies.

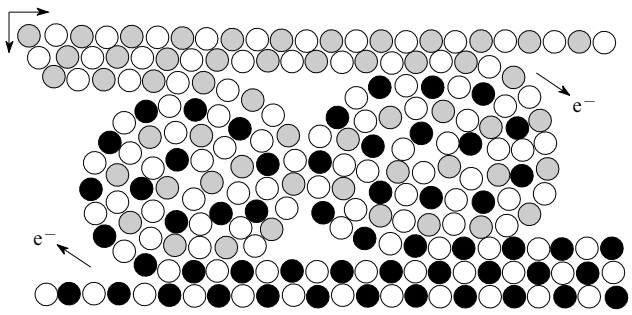


Figure 7. Dynamic state $(D)^*$ in the contact region between solid particles under loading.

Figure 8 presents the plot of the composition of a scheelite-type crystalline product *vs.* Mohs' hardness difference between reactants,[81] which was obtained from analysis of the intensities of X-ray reflections from the samples with conversions ranging from 0.5 to 0.9.

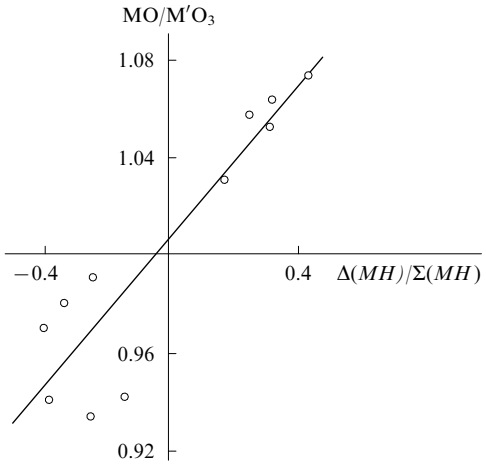


Figure 8. Compositon of scheelite-type crystalline product in the case of imcomplete conversion plotted *vs.* relative Mohs' hardness difference between reactants.[81]

Often, the primary product is not detected by powder X-ray diffraction owing to highly broadened peaks and low content. Equation (1) provides a simple explanation for a possible lack of products of mechanochemical reactions in the systems where solid-phase reactions readily occur on heating; the expression is also applicable to the case A = B (so-called mechanical activation). The plot of the relative density of $BaTiO_3$ *vs.* specific energy (Fig. 9) shows a dramatic decrease in the relative density (to 0.91) as a result of mechanical activation in an AGO-2 mill.[26] From geometric considerations it follows that the relative density of a product originating from (D)* should be about 0.90. A similar surprising coincidence with this numerical value of the relative density was also reported for mechanically activated quartz.[8] Mechanical treatment of polymers leads to significant structural loosening.[8] In δ-Bi_2O_3-based fluorites prepared by mechanochemical synthesis [24] the proportion of vacant oxygen positions is at most 17%, whereas the total concentration of only one type of

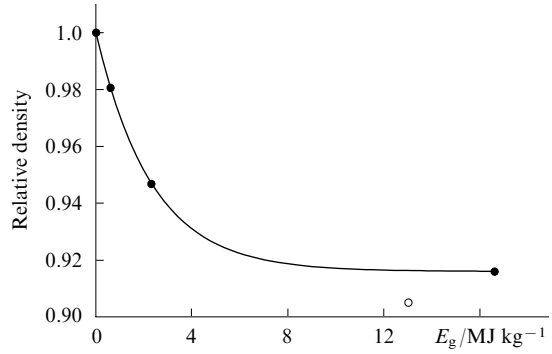


Figure 9. Relative density of $BaTiO_3$ plotted *vs.* specific energy on mechanical treatment in AGO-2 mill.[26]
Open circle indicates the data reported in Ref. 29.

structural defects, namely, vacancies in the Aurivillius phase exceeds 20%.[82]

Ultrahigh concentration of vacancies in oxides after intensive mechanical treatment first of all predetermines unusual structural, spectral, physical and chemical properties as well as thermal behaviour and sintering of these systems. The effective Mohs' hardness of mechanically activated oxides considerably decreases (by about a unity), which offers a unique possibility of controlling the structural type of the primary product.[26, 29] Large plastic deformations of solids cause the appearance of rotation domains that lead to structural loosening.[83, 84] The rotation and anisotropic domains appear even on shear loading of simple liquids, which gives rise to the so-called Couette flows.[85] The roller model was used for explanation of nucleation in plastic flow.[86]

The secondary loading events involve transformations with participation of products of mechanochemical synthesis and reactants after loading. Equation (1) is also applicable to the secondary events where the composition of the product of mechanochemical synthesis gradually approaches the composition of the mixture. However, the threshold character of the process causes the probability of formation and the size (D)* to dramatically decrease owing to the small contribution of the enthalpy of the process to ΔT^*. Eventually, the yield decreases by 1 to 2 orders of magnitude. The secondary processes can be described in terms of the so-called deformation mixing [12] with diffusion in the relaxation step. In any case, mass transfer through diffusion during relaxation (D)* owing to short distances (crystallite size of about 10 nm) and ultrahigh concentration of vacancies contributes largely even at $\Delta T_z \sim 200$ K.

The secondary events also include processes similar to coalescence

$$A_{1-\delta}B^* + A_{1-\delta}B^* \longrightarrow [A_{1-\delta}B^*],$$

which makes it possible to detect the low-yield products of mechanochemical synthesis by diffraction techniques. Bokhonov *et al.*[87] studied these processes in mechanically treated nanopowders prepared by other methods and observed an increase in the crystallite size by transmission electron microscopy (TEM). The process occurring at room temperature is similar to crystallisation, but has some specific features. The key role is apparently played by co-operative 'adjustment' of nanoparticles to one another, which is favoured by the periodic crystal field near the particle boundaries (Fig. 10). At loading, densification of the powder occurs, the pore size decreases and numerous interparticle contacts are formed.

Mechanical energy supplied is stored in the sample mainly in the form of (i) elastic energy, (ii) energy of grain boundaries and (iii) energy of point defects including charged ones. At unloading under negative pressure (see Fig. 4), random favourable orientations of crystallites in the ensemble are retained in the more ordered state (in terms of long-range order) owing to transformation of the energy stored to heat including electron–hole recombination, local release of the heat of 'crystallisation' (this potential energy was stored in the powder before loading). Ultrahigh concentration of vacancies favours reorientation of crystallites (owing to activated surface diffusion), namely, steric hindrances to rotation of particles are eliminated. Under unloading, anisotropic nanoparticles are under the 'boiling bed' conditions. The secondary events cause disintegration of large crystallites during the loading event and formation of other crystallites (on the average, of the same size) during the relaxation step. This dynamic equilibrium was analysed by Butyagin;[88] it is essentially similar to Huttig's

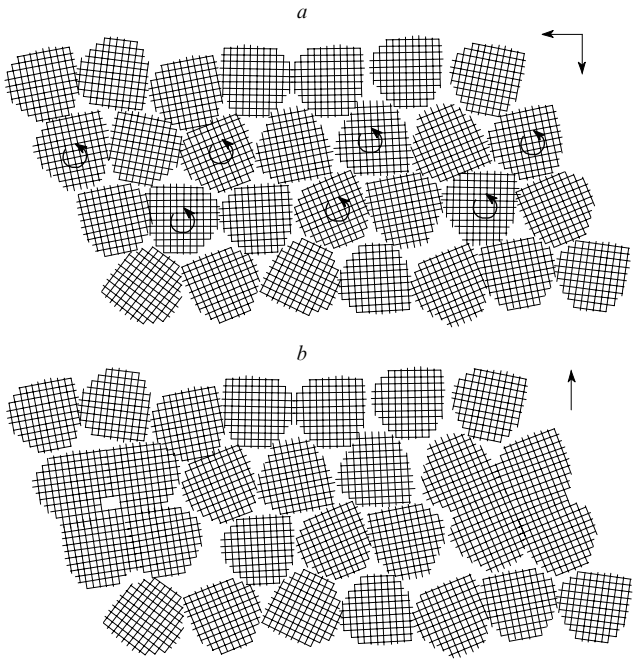


Figure 10. Growth of crystallites (coalescence) on mechanical treatment. At loading (*a*) and on unloading (*b*).

equilibrium in grinding (see Ref. 1). Here, an important feature should be emphasised, namely, the starting nanocrystals prepared by other methods have a relative density of $0.99 < \rho < 1$, which is typical of crystals; the density of crystallites under dynamic equilibrium on intensive mechanical treatment is only about ~ 0.9 (see Fig. 9).

Yet another important feature is as follows: the probability for the particles with cubic symmetry of the crystal lattice to have 'favourable' orientations in the ensemble is much higher than for the particles of low symmetry. Therefore, most complex crystalline oxides prepared by mechanochemical synthesis have cubic symmetry and are characterised by a maximum size of coherent scattering domains (CSD), up to 100 nm (for sillenites).[26]

Ultrafast mechanochemical reactions, *e.g.*,

$$PbO + MoO_3 \longrightarrow PbMoO_4$$

are characterised by immediate formation of rather large crystallites; as a result, the widths of the peaks in the X-ray diffraction patterns vary only slightly in the course of treatment.[89] Estimates [20, 29] for the fastest reactions of mechanochemical synthesis of complex oxides showed that a rotating roller (see Fig. 7) removes a monolayer from reactants with similar hardnesses, *i.e.*, there exists an upper limit for mass transfer through rolling (in contrast to mass transfer through diffusion). A mechanism was proposed, according to which monophase powders prepared by mechanochemical synthesis should in fact represent nanocomposites comprised of more ordered domains distributed in some way within an amorphous (disordered) matrix whose composition differs from the composition of the ordered domains. Indeed, the 'core–shell' structure of complex oxides was observed in all systems studied by high-resolution electron microscopy (HREM).[22, 32, 90–94] The dynamics of ultrafast mechanochemical synthesis (impact time scale of the order of 10^{-5} s) is about nine orders of magnitude faster than the possible rate of synthesis proceeding by the diffusion mechanism at the equilibrium concentration of

vacancies.[18] Therefore, inhomogeneity of the chemical composition and disordering of the phases prepared by mechanochemical synthesis is inevitable 'cost' of ultrafast mass transfer. For instance, inhomogeneity of the chemical composition of a fluorite-type complex oxide

$$2\,PbO + Sb_2O_3 \longrightarrow Pb_{0.5}Sb_{0.5}O_{1.25}$$

was estimated[95] from the compositions of the four phases formed in the decompositon of the metastable product after annealing under mild conditions. Assuming that mass transfer through diffusion has little effect on the inhomogeneity of the samples, the Pb : Sb ratio was found to vary from 0.5 to 2.0. The crystallite sizes determined using the Scherrer relationship from the broadening of the peaks in the X-ray diffraction pattern and by TEM were nearly equal (usually, tens of nanometres).[96, 97] However, HREM studies of certain complex oxides revealed structuring (Fig. 11),[91, 92] which was ascribed to 2–3-nm paracrystals (domains, twins, modulated domains). A study[96] of Sc-stabilised zirconium ceramics sintered to the dense state at 1640 K from powders prepared by mechanochemical synthesis led to amazing result, namely, an abnormally high low-temperature oxygen conductivity. This was attributed to nanostructuring of ceramics that 'remembers' the inhomogeneity of the powders prepared by mechanochemical synthesis after fast sintering at high annealing temperatures.

The dynamics of mechanochemical synthesis and the order of phase formation cannot be understood without using the notions 'primary products' and 'secondary products'.[18, 26, 29] The composition and structural type of the primary product are determined by the hardness difference between the starting reactants. The primary products are characterised by high mechanochemical yield $(E_{1/2})^{-1}$ (half-conversion energy $E_{1/2}$ in the AGO-2 mills is $\approx 1-5$ MJ kg^{-1} at an average impact speed of ~ 4 m s^{-1}). The yield of the secondary products is lower and depends on the composition of the starting mixture ($E_{1/2} \approx 5-100$ MJ kg^{-1}). Complex oxides are always the secondary products prepared in lower yields. Emission processes in the course of mechanochemical synthesis were ignored, because their intensity measured with external detectors is very low due to fast reverse electron–hole recombination. However, the observation of mechanically induced electron–hole ferromagnetic resonance (this was confirmed by magnetic susceptibility measurements) in many high-purity dielectrics[26, 98–100] including anatase TiO_2 indicates a very high intensity of mechano-emission of electrons at loading, which is comparable with the dynamics of formation of the secondary products.[29] The giant-intensity ferromagnetic resonance spectra showed a strong dependence on the orientation of the samples compacted after pulsed mechanical loading.¶ After grinding of the samples the spectrum averaged over the angles but its intensity decreased considerably. Because of this similar spectra were not observed in numerous studies of paramagnetic centres that appear on milling.[101] A theoretically predicted[26, 29] new class of products prepared by mechanochemical synthesis (it is related to mechanolysis of oxides[102]) was obtained; the dynamics of mechanochemical synthesis in this case was quantitatively substantiated (Fig. 12). Unavoidable reduction of oxides during mechanical treatment in the oxidative medium is a specific feature of the mechanochemical approach (post-reactions with oxygen result in intermediate oxidation state). Note that the first four new compounds prepared by mechanochemical synthesis in the Ba–Cu–O,[19] La–Mo–O,[22] V–Mo–O (Ref. 25) and Zn–Mo–O systems represented the reduced phases.



Figure 11. A HREM image of a crystallite of $Bi_{1.5}Y_{0.3}Sm_{0.2}O_{3+x}$ fluorite prepared by mechanochemical synthesis.[91]

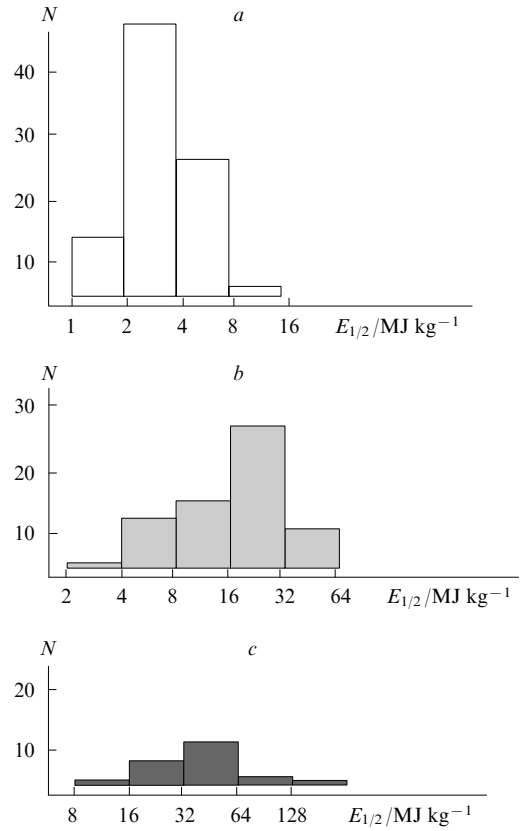


Figure 12. Half-conversion energy distribution of systems studied for the primary (*a*) and secondary (*b*) products of mechanochemical synthesis and for the phases reduced during mechanical treatment (*c*). *N* is the number of systems.

¶ A pressed disk-like sample (pellet) is in line with impact direction and 'remembers' this orientation, which manifests itself in spectra. Rotation of the disk in a magnetic field causes significant changes in the spectra.

IV. Comparing mechanisms of ultrafast mechanochemical synthesis in AGO-2 impact mills and in 'Fritsch' ball mills

Information on the mechanism of ultrafast mechanochemical synthesis of complex oxides was obtained in studies of powders treated under shock loading in home-made AGO-2 mills. These conditions are unattainable with the planetary mills available on the market. At the same time most studies were carried out with this type of mills. The problem of comparing the results obtained using different-type devices was posed by Butyagin long ago but still remains unsolved. Owing to pronounced threshold character of the process of ultrafast mechanochemical synthesis (half-conversion times from 30 to 600 s) the results (X-ray diffraction patterns) of conventional experiments on mechanochemical synthesis obtained at treatment durations from ~ 1 to 240 h are more suitable for interpreting. A practically important consequence of the theory of ultrafast mechanochemical synthesis is the possibility of making an optimal choice of systems for basic research and applications. Namely, the maximum yield should be expected in the mechanochemical reactions involving heavy metal oxides (first of all, the bismuth, lead and lanthanide oxides that are of practical interest). Indeed, the authors of more than 50% of the total number of publications in the field of mechanochemical synthesis of complex oxides report on successful (according to X-ray phase analysis data) observation of mechanochemical synthesis in the mixtures of oxides of these elements.

Experience has shown that the order of processes occurring during mechanical treatment in the AGO-2 mills is strongly different for different systems. Figure 13 presents the main types of the dynamics of the phase composition at a 1 : 1 atomic ratio of metal oxides in the mixture. Considering n curves of changes in the specific surface area for each type, one gets a total of $5n$ different situations, which seem to point to different reaction mechanisms. Actually, grinding is an independent process, which occurs concurrently with mechanochemical synthesis, in particular, at the boundaries of the reaction zone under ball-induced shock, or under rolling and attrition of powder. In some cases the specific surface area S_s decreases by more than an order of magnitude upon mechanical treatment,[103] but in other cases (*e.g.*, when adding an additive for preparation of a catalyst, it can increase by more than an order of magnitude.[104] In both cases mechanochemical synthesis occurs irrespective of the changes in S_s. For ultrafast reactions in the region of interparticle contacts with rolling mass transfer mechanism the change in the dispersion has almost no effect on the final results.

In the text below we present some examples of chemical reactions that can be described using the 'kinetic' curves shown in Fig. 13.

The first type (see curve *1*) corresponds to the reaction

$$PbO + MoO_3 \longrightarrow PbMoO_4 .$$

Here the reactants are similar in hardness, have high molecular masses, the yield is high and there exists a scheelite-type phase having the same structural formula as the composition of the mixture.

The second type (see curve *2* in Fig. 13) corresponds to the reaction

$$PbO + TiO_2 \longrightarrow PbTiO_3 ,$$

in which the reactants are strongly different in hardness, the primary product with high PbO content is structureless; the final product with the perovskite structure is formed as a result of secondary loading events and gradual coalescence from the amorphous state. A similar kinetic curve corresponds to the reaction

$$MgO + TiO_2 \longrightarrow MgTiO_3 .$$

Here the reactants have the same hardness, but low molecular masses; therefore, the yield is low and the final product can only be formed as a result of gradual coalescence from the amorphous state.

The third type (see curve *3* in Fig. 13) corresponds to the reaction

$$PbO + WO_3 \longrightarrow PbWO_4 ,$$

in which the reactants are strongly different in hardness and have high molecular masses. Therefore, the yield is high, but the primary product is Pb_2WO_5, while the final, secondary product is formed in the reaction

$$Pb_2WO_5 + WO_3^* \longrightarrow PbWO_4 .$$

The fourth type (see curve *4*) corresponds to the reaction

$$2\,Bi_2O_3 + 4\,GeO_2 \longrightarrow Bi_4Ge_3O_{12} + GeO_2\ (\text{amorphous}).$$

Germanium dioxide is harder than bismuth oxide, the molecular masses of the reactants are high and therefore the

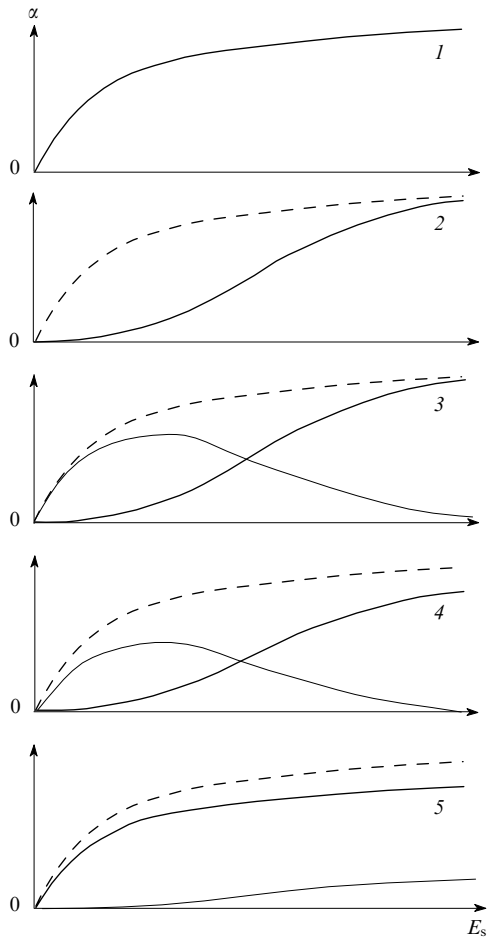


Figure 13. Typical 'kinetic' curves for mechanochemical synthesis (solid lines) and consumption of the starting oxides (dashed lines) according to X-ray diffraction data of crystalline products.
For curves (*1*–*5*), see text; α is the degree of conversion.

yield is high; but the primary product is the Aurivillius phase Bi_2GeO_5, which is transformed to eulytite in the secondary loading events following the reaction

$$2\,Bi_2GeO_5 + GeO_2^* \longrightarrow Bi_4Ge_3O_{12}\,.$$

The fifth type (see curve *5*) characterises a complex phenomenon, namely, a mechanochemical equilibrium,[105–108] which is an analogue to tribochemical equilibrium between different structures of the same composition (see Refs 1, 2 and 109). For the 1 : 1 composition, an example is provided by the reaction

$$Bi_2O_3 + 2\,VO_2 \longrightarrow BiVO_{3.5} + Bi_2VO_5\,,$$

in which the reactants are similar in hardness and have high molecular masses; therefore, the yield is high. But eventually an equilibrium is attained between the primary (major) clinobisvanite-type phase $BiVO_{3.5}$ and the Aurivillius phase Bi_2VO_5. It was reported [26, 29] that the mechanochemical equilibrium is a result of the competition between structural types for the reactant that is in deficiency in the amorphous state; this occurs during relaxation upon the secondary loading events.

Researchers who use the Fritsch mills in studies on new systems first of all observe changes in the X-ray diffraction patterns with the duration of mechanical treatment. If the intensity of loading is insufficient, the most part of the variety of mechanochemical transformations (see Fig. 13) is not detected, because X-ray amorphous or poorly crystallised products provide no information on the sequence of mechanochemical reactions. Usually, the X-ray diffraction patterns are used to confirm the one-step mechanochemical synthesis even with three and more reactants, because peaks of products appear against the halo from X-ray amorphous state and increase with treatment duration and become narrower due to better mixing of reactants on the atomic level and gradual coalescence. If the impact energy is insufficient to overcome the threshold (see Fig. 6), mechanochemical synthesis occurs steadily and the energy is accumulated in the system in the following order: grinding and mixing of reactants → aggregation of particles → deformation mixing on atomic level → formation of amorphous state → coalescence to give a product detectable by powder X-ray diffraction (narrowing of X-ray reflections) → amorphisation owing to reduction of oxides on prolonged mechanical treatment. Of course, energy expenditure for grinding is relatively high (mechanical treatment takes a rather long time). Therefore, the use of precursors (*e.g.*, preground powders) significantly accelerates mechanochemical synthesis. In many cases including the atomic ratios different from 1 : 1, high molecular masses of reactants or strong influence of enthalpy (in the reactions with BaO, SrO and CaO), intermediate situations are possible, where powder X-ray diffraction data will point to some manifestation of the types of the dynamics of phase composition shown in Fig. 13. This was observed [31] for the reaction

$$2\,SrO + TiO_2 \longrightarrow SrTiO_3 + Sr_2TiO_4\,.$$

Mechanochemical synthesis in this mixture is characterised by the fifth type of dynamics (see Fig. 13), namely, similarity between the oxide hardnesses and high tolerance cause initially the formation of perovskite $SrTiO_3$ whose complete transformation to a layered Sr_2TiO_4 structure is impossible because of the dynamic equilibrium established at this energy of mechanical pulses. The perovskite structure is kinetically more preferable upon relaxation of (D)*, whereas the layered Sr_2TiO_4 phase is present among reaction products because its composition matches that of the mixture. Traces of the Sr_2TiO_4 phase were detected by HREM. Usually, the mass balance equations written for mechanochemical transformations do not describe them correctly because a fraction of the material remains in the amorphous state and the ordered domains have highly non-stoichiometric compositions.

It should be noted that sometimes mechanochemical transformations should not occur from thermodynamical considerations; nevertheless, they do occur. This is due to the open character of the systems in question. For instance, mechanochemical reactions of hydrated compounds, hydroxides and even salts begin with mechanically activated dehydration (decomposition) followed by the reaction of the ground reactant (in fact, it has a different composition). Here, a crucially important role is played by the atmosphere within the drum, which is determined by the possibility of exchange with the environment (no exchange if milling occurs in hermetically closed drums). Provided conservation of the composition of solid reactants a structural transformation (mechanical activation) with a decrease in the effective hardness can occur in the initial step. Gradual accumulation of different forms of energy in solid reactants can result in the mechanochemical synthesis reaction. Important details of the experimental procedure are often not reported owing to misunderstanding of the mechanism of mechanochemical synthesis.

V. Structural types of complex oxides prepared by mechanochemical synthesis

Strictly speaking, metastable products with crystallite sizes less than 100 nm (usually, 20–30 nm) prepared by room-temperature mechanochemical synthesis cannot be treated as conventional 'phases'. Indeed, they have no well-defined composition and interfaces (diffuse boundaries) and their parameters depend on the experimental conditions. These products cannot also be considered as crystalline compounds, because the translation probability (translation is the main symmetry operation) is often lower than 0.5. The concentrations of structural, antistructural, electron and other types of defects in such systems are so high that the notion 'defect' becomes senseless.

In inorganic crystal chemistry the minimum of the energy of the atom–atom interaction predetermines the structure and properties of the entire crystal. Contrary to this, weakly ordered products prepared by mechanochemical synthesis and showing X-ray diffraction patterns have a high excess energy and loose packing. All mechanochemically synthesised compounds can be treated as 'pseudocrystalline'. The term 'anti-glass' proposed in joint studies [110, 111] of mechanochemically synthesised compounds by spectral, magnetic and X-ray diffraction methods carried out to characterise structural disordering in these systems points to a high extent of long-range order and a poor short-range order in these compounds.

To a first approximation, the best strategy of investigations of compounds prepared by mechanochemical synthesis and showing X-ray diffraction patterns is to determine the most probable spatial arrangement of heavy atoms by routine methods. However, many known features of mechanochemically synthesised compounds (electronic substructure, electron density modulations, radicals and clusters, low density) do not manifest themselves in X-ray diffraction patterns. Therefore, characterisation of such compounds using a single method will only artificially restrict the description of their amazing properties. Local 'distortions' in nanosized non-stoichiometric materials are intrinsic in nanostructures and can cause the appearance of extra peaks in diffusive scattering patterns.

Novel methods have been developed to analyse such nanostructured materials that are first of all of interest for catalysis.[112, 113] They were evaluated on rather simple systems and showed the possibility of extracting additional information (in particular, concerning partial ordering of planar defects and methods of twinning). At present, these methods are of limited use; however, in the future they will provide a basis for the next step in characterisation of compounds prepared by mechanochemical synthesis.

1. Perovskites

A large number of mechanochemically synthesised compounds belongs to perovskites, which is due to high tolerance this structural type. Perovskites prepared by mechanochemical synthesis can be classified as follows: PbO-containing piezoelectrics; known ferroelectric compounds; conducting perovskites and perovskites having novel and unusual compositions.

When fabricating lead-containing piezoelectric materials, one of the key problems consists in evaporation of PbO during the synthesis and sintering. Therefore, considerable literature is devoted to mechanochemical synthesis (no calcination) of sintering-ready ceramic nanopowders. In addition, the powders prepared by mechanochemical synthesis have reduced sintering temperatures. The Bi- and Pb-containing systems should have a high yield (low threshold) even if the enthalpy of reaction has little effect.[18, 26, 29] Indeed, PbO-based perovskites can be mechanochemically synthesised by prolonged milling in conventional laboratory mills with ceramic balls.

Wang *et al.*[114, 115] discovered the formation of lead titanate (crystallite size 20–30 nm) after milling of a mixture of starting oxides for 10 h and reported a new method of synthesis. This gave an impetus to studies on mechanochemical synthesis of numerous complex perovskites of similar compositions. However, the first monophase samples of lead titanate mechanochemically synthesised from different structural modifications of oxides were prepared much earlier.[19, 68] The structure and the effect of annealing on the structure of these samples were thoroughly investigated more recently.[116] The use of various combinations of starting reactants including oxide polymorphs, hydrated compounds and hydroxides to control mechanochemical synthesis of a single compound has become a routine technique, which is especially efficient when using mills with shock intensity lower than the threshold value.

Now we will consider the most important general results obtained for oxide mixtures in the model system Pb–Ti–O after intensive treatment in an AGO-2 mill for ~30 min with minimum contamination (< 0.05 mass %) followed by reduction of samples. This seems to be appropriate because in almost all studies the product composition determined by X-ray phase analysis is by default assumed to be the same as the composition of the starting mixture even when analysing samples (i) with high degree of amorphisation and (ii) whose unit cell parameters differ appreciably from those of the equilibrium phases. Data on the dynamics of mechanochemical synthesis for different phase combinations of the starting mixture with the Pb : Ti = 1 : 1 atomic ratio (including minium Pb_3O_4) are listed in Table 3. Comparison with thermal synthesis studied using the same phase combinations and narrow submicron fractions of powders at low temperatures (below the litharge-to-massicot transition temperature)[117] revealed strong differences in the relative reactivities of the phase combinations.

Table 3. Dynamics of mechanochemical synthesis of perovskite from Pb–Ti–O system oxides with different Mohs' hardness.

Lead oxide		Titania		$E_{1/2}$ / MJ kg^{-1}
name	*MH*	name	*MH*	
Massicot	2	anatase	5	15 (3)
		rutile	6	30 (6)
Litharge	2	anatase	–	18 (4)
		rutile	–	40 (8)
Minium	3	anatase	–	18 (4)
		rutile	–	19 (4)

The parameters of the perovskite structures in $PbO + TiO_2$ mixtures [a = 3.896(4), c = 4.136(5) Å, c/a = 1.062] determined at low energy supplied ($E_s \sim 5$ MJ kg^{-1}) are strongly different from the corresponding parameters of $PbTiO_3$ (a = 3.8993, c = 4.1532 Å, c/a = 1.065, PDF 6-452). All phases prepared by mechanochemical synthesis were analysed using the same (average) model structure; variations of structural parameters of crystallites due to inhomogeneity of composition were ignored. In the X-ray diffraction patterns of systems containing minium, the peaks of reactants and products overlap only slightly; therefore, more detailed information on the composition of crystallites was obtained assuming a constant composition with respect to oxygen (Table 4). The perovskite is deficient with respect to the solid reactant TiO_2, while the presence of a minor concentration of rutile was established by X-ray phase analysis even at high energy supplied.

At E_s = 30–60 MJ kg^{-1}, no marked changes in the X-ray diffraction patterns are observed. These samples allow the structural parameters of perovskite to be determined more precisely (Table 5, 6). The structural parameters of the compositions minium + anatase (rutile) and anatase + massicot (litharge) are almost identical.

Table 4. Structural parameters of perovskites prepared by mechanochemical synthesis from mixtures of minium with anatase and rutile (E_s = 10 MJ kg^{-1}); determined from eight X-ray reflections.

The unit cell parameters			Structural formula	Pb : Ti	B position coordinates			R (%) (see [a])
a / Å	c / Å	c/a			x	y	z	
Minium + anatase								
3.910(3)	4.215(5)	1.078	$(Pb^{2+}_{0.69}Pb^{4+}_{0.14})(Pb^{4+}_{0.2}Ti_{0.71})O_2O_{0.8}$	1.45	0.5	0.5	0.5	2.0
Minium + rutile								
3.912(3)	4.203(5)	1.074	$(Pb^{2+}_{0.75}Pb^{4+}_{0.03})(Pb^{4+}_{0.345}Ti_{0.55})O_2O_{0.6}$	2.05	0.5	0.5	0.5	9.7

[a] Reliability factor.

Table 5. Parameters of mechanochemical synthesis of perovskites at $E_s = 60$ MJ kg^{-1}.

The unit cell parameters			Structural formula	Pb : Ti	B positon coordinates			CSD size/nm	
a/Å	c/Å	c/a			x	y	z	D_a	D_c
Minium + TiO_2									
3.904(3)	4.170(4)	1.068	$(Pb_{0.727}Pb^{4+}_{0.239})(Pb^{4+}_{0.125}Ti_{0.753})O_2O_{0.96}$	1.45	0.5	0.5	0.54	36	34
PbO + anatase									
3.913(3)	4.089(4)	1.045	$(Pb_{0.96})(Pb^{2+}_{0.096}Ti_{0.862})O_2O_{0.78} \div (Pb_{0.96})(Pb^{2+}_{0.074}Ti_{0.893})O_2O_{0.82}$	1.19(3)	0.5	0.5	0.54	30	25

Table 6. Observed (I_{obs}) and calculated (I_{calc}) X-ray reflection intensities of perovskites prepared by mechanochemical synthesis at $E_s = 60$ MJ kg^{-1}.

$h\ k\ l$	Minium + TiO_2		PbO + anatase	
	I_{obs}	I_{calc}	I_{obs}	I_{calc}
0 0 1	18	17	17	17
1 0 0	25	25	30	30
1 0 1	100	100	100	100
1 1 0	44	45	44	44
1 1 1	28	29	31	31
0 0 2	13	13	12	12
2 0 0	27	27	27	27
1 0 2	11	11	11	11
2 0 1	8	8	8	8
2 1 0	7	6	8	8
1 1 2	23	22	21	22
2 1 1	37	38	39	39

Table 8. Observed (I_{obs}) and calculated (I_{calc}) X-ray reflection intensities of perovskites prepared by mechanochemical synthesis after annealing for 30 min.

$h\ k\ l$	Minium + TiO_2		PbO + anatase	
	I_{obs}	I_{calc}	I_{obs}	I_{calc}
3 0 0	12	–	–	–
0 0 1	12	13	15	15
1 0 0	19	19	32	31
1 0 1	100	100	100	100
1 1 0	44	45	40	39
1 1 1	27	26	29	31
0 0 2	12	13	11	12
2 0 0	27	28	26	27
1 0 2	8	9	11	11
2 0 1	7	6	8	7
2 1 0	5	5	8	7
1 1 2	20	22	20	20
2 1 1	38	38	38	39

The reliability factors R are not shown in Table 5, because the number of parameters was only slightly smaller than the number of peaks observed. Owing to inhomogeneity and small number of peaks observed the structural parameters of mechanochemically synthesised nanopowders are determined much less reliably than those of the powders prepared by conventional techniques. The reliability of determination can be improved, in particular, by performing a large number of independent determinations of structural parameters of different samples and by revealing trends of their changes on, *e.g.*, annealing and using the full-profile Rietveld analysis. A low population of B positions by Pb^{2+} ions should be pointed; this is atypical of crystal chemistry of perovskites and is independently confirmed by the numerical value of the unit cell parameter a.

Perovskite structures become much more ordered on low-temperature annealing at 573 – 673 K (Tables 7, 8); first of all the number of lead atoms in the 'alien' B positions decreases. Annealing causes the CSD size to increase due to the diffusion of excess PbO in the perovskite towards X-ray amorphous environment containing an excess of TiO_2. As a result the overall content of structural vacancies increases, the blocks become more isotropic ($D_a \sim D_c$) and the Pb : Ti ratio approaches a unity. The perovskites annealed at $\sim$800 K have the structural formula $PbTiO_3$.

Annealing of minium samples leads to appearance of two narrow extra peaks at 7.14 (strong) and 3.57 Å (weak) in the X-ray diffraction patterns in the temperature range 623 – 723 K. The peaks were ascribed to incommensurate phase with the superlattice $a^* = 4\sqrt{2}ka$, where $k = 0.97$.[116] The appearance of electron density modulations that give rise to the incommensurate superlattice is associated with ordering of relatively small Pb^{4+} ions in the A positions. The possibility of formation of incommensurate phases in $PbTiO_3$ was predicted three decades ago.[118] Incommensurate modulations are sometimes observed in solid solutions whose components have strongly different ionic radii due to ordering of small polyhedra, *e.g.*, the CrO_4^{2-} tetrahedra in the fluorite-type $Bi_{1-x}Cr_xO_{1.5+1.5x}$.[119] The data on PbO-containing piezoelectrics and ferroelectrics obtained by mechanochemical synthesis are listed in Table 9.

Table 7. Parameters of perovskites prepared by mechanochemical synthesis ($E_s = 60$ MJ kg^{-1}) after annealing for 30 min.

T/K	The unit cell parameters			Structural formula	Pb : Ti	B position coordinates			CSD size /nm	
	a/Å	c/Å	c/a			x	y	z	D_a	D_c
Minium + TiO_2										
673	3.904(3)	4.152(4)	1.064	$(Pb_{0.663}Pb^{4+}_{0.202})(Pb^{4+}_{0.129}Ti_{0.817})O_2O_{0.96}$	1.22	0.5	0.5	0.54	53	51
PbO + anatase										
623	3.906(3)	4.089(4)	1.047	$(Pb_{0.8})(Pb^{2+}_{0.044}Ti_{0.828})O_2O_{0.5} \div (Pb_{0.8})(Pb^{2+}_{0.037}Ti_{0.893})O_2O_{0.52}$	1.01(3)	0.5	0.5	0.54	32	32

Table 9. Data on mechanochemical synthesis of PbO-based perovskites.

Composition		Crystallite size /nm	Treatment duration /h	Composition (X-ray phase analysis data)	Ref.
starting mixture	abbreviation				
$PbO(1/3\,Pb_3O_4) + TiO_2$	PT	30 – 50	0.5	monophase	19, 68, 116
		10 – 20	20 – 48	"	115, 120
$PbO + ZrO_2$	PZ	20	–	multiphase	121
$PbO + ZrO_2 + TiO_2$	PZT	–	–	amorphous	122, 123
		20	–	multiphase	124
				amorphous-like	120
		~10	1	multiphase	125, 126
		30 – 50	–	monophase from amorphous precursor	127
$Pb(Mg_{1/3}Nb_{2/3})O_3$	PMN	~10	20	monophase	128, 129
$Pb(Mg_{1/3}Nb_{2/3})O_3$ + + $PbO(1/3\,Pb_3O_4) + TiO_2$	PMN + PT	–	–	–	128 – 134
$Pb(Zn_{1/3}Nb_{2/3})O_3$	PZN	35 – 41 [a]	0.5	–	135
		70 – 79 [b]	0.5	–	135
$Pb(Zn_{1/3}Nb_{2/3})O_3$	PZN	~10	20	monophase	124, 136 – 140
$BiFeO_3 + PbO(1/3\,Pb_3O_4) + TiO_2$	BF + PT	20 – 35	8	"	141
$Pb(Fe_{2/3}W_{1/3})O_3$	PFW	20 – 30	5	monophase from amorphous precursor	142
$Pb_{0.92}La_{0.08}Zr_{0.65}Ti_{0.35}O_3$	PLZT	~10	36	–	143, 144
$Pb_{0.4}Ca_{0.6}Fe_{0.5}Ta_{0.5}O_3$	PCFT	–	60	monophase	145
$0.9\,PbO + 0.1\,CaO + TiO_2$	–	–	–	"	146

[a] For perovskite. [b] For pyrochlore.

Researchers in different laboratories prepare powders for piezoceramic materials based on PbO-containing perovskites in different manner, namely, by mechanical treatment of amorphous precursors,[142] by mechanochemical synthesis from complex oxides,[145] by soft mechanochemical synthesis [147] and starting from carbonates [145] and hydroxides.[134] The quality of such powders should be compared using the main characteristic, that is, the parameters of the target ceramics. It is of great importance to remove chemisorbed water and acid residues from such powders (especially, nanostructured ones) prior to densification; otherwise, pores will close and dilation effects will manifest themselves on sintering. Using soft methods of synthesis from carbonates, chlorides and hydroxides, one can prepare powders of desired composition (according to powder X-ray diffraction data) rather than ceramics that are ready for sintering. Pre-calcination leads to the loss of an advantage of the mechanochemical method, namely, all studies on mechanochemical synthesis of ceramic oxides point to importance of exclusion of the calcination step accompanied by evaporation of lead oxide and violation of stoichiometry, which deteriorates the properties of the final product, *i.e.*, ceramics. In addition, the sintering of powders is improved when carried out at reduced temperatures relatively to the traditional ceramic technology. However, the quantitative characteristics of ceramics are not always improved; only a few parameters are affected. Kong *et al.* reported [139, 144] mechanochemical synthesis of high-quality nanopowders of compositions PMN and PMN – PT for preparation of transparent ceramics.

Aggregation of powders in the course of mechanochemical synthesis is unavoidable. When using the Fritsch mills, the aggregate size is usually at most 10 μm. There is a clear correlation, namely, the faster the mechanochemical synthesis of the complex oxide the more aggregated the nanopowders. The morphologies of different fractions of oxide powders prepared in the AGO-2 mills were studied in detail using adsorption and microscopy methods.[19, 20, 26, 27] It was found that nanocrystallite aggregates have a relative density of ~0.8, being less than 2 μm in size. They form secondary agglomerates of size 2 – 100 μm and a relative density of ~0.7. This morphology is stable for many simple and complex oxides treated in AGO-2 and similar mills.

Preparation of ceramics from highly aggregated powders usually gives negative results because high activity of particles in sintering and high inhomogeneity of compacts eventually lead to formation of ceramics with low density (<0.95) and highly inhomogeneous granular composition. This is a well-known phenomenon of zone separation on shrinking, which is called 'the Bal'shin law' in domestic literature on the subject.[148] When compacts contain agglomerates of size up to 100 μm, the formation of pores a few tens of micrometres in size is possible; these pores do not disappear even after prolonged calcination. Fractionation of powders using an electro-mass-classifier [51] and investigations of thermal and radiation-thermal sintering of complex oxides having different pre-histories in mono- and bimodal compositions with controllable granulometric composition was studied.[149 – 155] Mild sintering of a submicrometre fraction comprised of dense aggregates gave a dense ceramics. This approach makes it possible to control the morphology and properties of ceramics over a wide range.[154, 155] The proportion of this fraction is only 5% – 10%; however, its activity in sintering normalised to S_s is higher than the activities of powders prepared by other methods. This is due to high concentration of vacancies, which cannot be completely annealed under optimal calcination regime.[26] The use of fractionated nanopowders obtained by mechanochemical synthesis allows one to prepare ceramics whose quality is as high as the quality of ceramics prepared by modern 'wet' methods, but in the former case the product is cheaper and has a lower shrinkage owing to better compaction of the fractionated powders.

Oxides $Pb(B^{2+}_{1/3}B^{5+}_{2/3})O_3$ showing a diffuse ferroelectric phase transition are of the greatest scientific and technological interest. These compounds were first synthesised by Smolenskii in the 1950s;[156] however, they have found practical applications only recently. This is due to complicated synthesis of monophase perovskite ceramics, especially $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN), which was prepared only as single crystals. Microinhomogeneity of the chemical composition predetermines excellent piezoelectric properties of relaxor materials, but precludes preparation of ceramics with reproducible properties, especially with allowance for the loss of PbO. To show the relaxor properties, the perovskite B positions responsible for the formation of polar domains in the non-polar matrix should be occupied by differently charges cations.[157] The nature of the polar domains is debatable and there are opposite strategies of materials design. For instance, Politova *et al.*[158] introduced a $Pb(Mg_{1/2}W_{1/2})O_3$ additive characterised by ordering of the magnesium and tungsten cations to increase the number of ordered domains in the PMN – PT ceramics. Contrary to this, the optimal (for manifestation of electrophysical properties) extent of disordering in the B-sublattice reported by Gao *at al.*[159] was attained by mechanochemical synthesis of disordered perovskite $Pb(Sc_{1/2}Ta_{1/2})O_3$ followed by heat treatment of the compound.

We have also studied the mechanochemical synthesis and properties of ceramics in one of the most promising compositions, $0.9\,PZN - 0.1\,ABO_3$, near the morphotropic phase boundary.[135] The results obtained are listed in Table 10.

The phase composition of the product is strongly dependent on the procedure for mechanochemical synthesis, on the pre-annealing and on other operations. A very high degree of instability of PZN was confirmed. The only additive suitable for full stabilisation of the perovskite structure of PZN both in the course of mechanochemical synthesis and after heat treatment in any fashion is $BaMnO_3$.[134] In other studies the perovskite structure of PZN was only stabilised using a large number of additives. According to powder X-ray diffraction data, the characteristic crystallite size is 35 – 40 nm for perovskites and 70 – 80 nm for pyrochlores prepared by mechanochemical synthesis. Also, powder X-ray diffraction showed that all perovskites studied retain cubic symmetry after annealing, although the morphotropic phase boundary passes between the rhombohedral and tetragonal structures.[160] Probably, this is the reason why ceramics having a high relative density (0.97) and prepared by rapid sintering at a reduced temperature (1323 – 1373 K, *cf.* 1423 K for conventional powders) have much lower dielectric permittivities and possess the properties typical of relaxor ferroelectrics.[161]

Despite a dramatic shortening of treatment duration and reduction of the calcination temperature upon sintering the loss of lead oxide through sublimation does occur for PbO-based perovskites derived by mechanosynthesis. High volatility of oxides after intensive mechanical treatment was observed in many cases, namely, for the iron, cobalt and zinc oxides from ZrO_2-based ceramics,[96] zinc oxide from ZnO-based ceramics [163] and bismuth and lead oxides from sillenites.[162] This is due to the presence of low-coordinate metal atoms (in clusters, radicals, in the crystal lattice of solids) owing to high concentration of vacancies. This effect is similar in nature to the shifts of bands in the optical absorption spectra of MgO[8] and in the photoelectron spectra of bismuth (they are associated with a decrease in the bond energy).[108] This feature of the mechanically activated powders was employed for accelerated growth of ZnO nanowires.[163] The data on mechanochemical synthesis of perovskite dielectrics are listed in Table 11.

Table 10. Phase composition and the perovskite and pyrochlore unit cell parameters in samples of heat treated PZN-based ceramics prepared by mechanochemical synthesis.[135]

Composition and pattern of mechanochemical synthesis	The unit cell parameter after mechanochemical synthesis /Å		The unit cell parameter after annealing /Å		Perovskite content		
	perovskite	pyrochlore	perovskite	pyrochlore	after mechanical treatment	after annealing	T/K
P + Z + N	4.063	10.597	4.046	10.575	0.60	0.12	1323
P + ZN	4.062	10.590		10.577	0.07	0.0	1323
P + Z + N + $PbTiO_3$	4.057	10.584	4.043	10.567	0.75	0.41	1323
(P + ZN) + $PbTiO_3$	4.055	10.578		10.560	0.25	0.00	1323
P + Z + N + $BaTiO_3$	4.060	10.596	4.051	10.583	0.74	0.74	1323
(P + Z + N) + $BaTiO_3$	4.049	10.582	4.041	10.566	0.76	0.73	1323
P + Z + N + $SrTiO_3$	4.054	10.583	4.043	10.578	0.82	0.86	1323
P + Z + N + CaO + TiO_2	4.061	10.578	4.052	10.560	0.81	0.25	1323
P + Z + N + PbO + ZrO_2	4.067	10.621	4.065	10.615	0.88	0.67	1223
				10.634		0.00	1323
				10.635		0.00	1223 + 1073
P + Z + N + SrO + ZrO_2	4.057	10.604	4.057	10.633	0.89	0.77	1323
P + Z + N + $SrFeO_3$	4.057	10.600	4.040	10.593	0.88	0.82	1323
P + Z + N + $LaFeO_3$	4.055	10.603	4.036	10.585	0.90	0.69	1323
P + Z + N + $Sr_{0.5}La_{0.5}FeO_3$	4.054	10.592	4.044	10.595	0.91	0.68	1323
P + Z + N + $BiSbO_3$	4.082	10.649		10.579	0.61	0.00	1323
P + Z + N + $SrBiO_3$	4.071	10.653	4.054	10.608	0.95	0.61	1323
P + Z + N + $BaBiO_3$	4.077	10.676	4.069	10.626	0.96	0.64	1223
				10.631		0.00	873 + 1223
			4.067	10.619		0.66	1223 + 1073
			4.065	10.613		0.76	1323
P + Z + N + $BaMnO_3$	4.061		4.059	1.0	1.0	1323	

Note. Notations are as follows: P stands for PbO, Z stands for ZnO and N stands for Nb_2O_5.

Table 11. Data on mechanochemical synthesis of perovskite insulators.

Starting mixture	Treatment duration /h	Crystallite size /nm	Composition from X-ray diffractions data	Ref.
$MgO + TiO_2$		–	perovskite traces	164
$CaO + TiO_2$	100	11	monophase	164, 165
$SrO + TiO_2$	50	12	almost monophase	31, 164
$BaO + TiO_2$	50	12	the same	164, 166
$(1-x)BaO + x\,SrO + TiO_2$	–	–	amorphous + perovskite	167
$Na_2CO_3 + Nb_2O_5$	40	10–20	almost monophase	168
$Y_2O_3 +$ + $Al(OH)_3$ (Fe_2O_3)	24	25	amorphous + monophase	32

Compound $MgTiO_3$ cannot be prepared by mechanochemical synthesis in conventional planetary mills.[18] Despite a high effect of enthalpy, the alkali and alkaline earth metal oxides (especially BaO and SrO) are the least appropriate for mechanochemical synthesis owing to very high susceptibility to moisture and CO_2 (rapid carbonisation occurs). Direct mechanochemical synthesis of the perovskites listed in Table 11 is of no practical concern, because preliminary preparation of pure oxides requires prolonged calcination. This was also confirmed in a review.[169] Mechanochemical synthesis of Sr- and Ba-containing complex oxides should be performed using chemically bound oxides. Very high reactivity of Ba-, Sr- and Ca-based perovskites prepared by mechanochemical synthesis to moisture and carbon dioxide owing to high concentration of vacancies can appear to be useful for the use of these compounds as absorbents. Carbonate impurities make the powders prepared by mechanochemical synthesis inappropriate for preparation of dense ceramics.

As regards the number of mechanochemically synthesised compounds studied, perovskites possessing high electron and mixed conductivities rank first (Table 12). This is due to their wide use for preparation of dense and porous ceramics employed in fabrication of solid oxide fuel cells (SOFC), catalytic membrane reactors (CMR), oxygen separators and other electrochemical devices, catalysts, *etc*.

Table 12. Data on mechanochemical synthesis of conducting perovskites.

Starting mixture	Treatment duration /min	Crystallite size /nm	Composition from X-ray diffraction data	Ref.
$La_2O_3 + Co_2O_3(Fe_2O_3)$	180–1440	~15	monophase	104, 170–172
$La_2O_3 + Mn_2O_3$	180	~20	"	173
$SrO(La_2O_3) +$ + $Mn_2O_3(MnO_2)$	–	–	"	174
$La_2O_3(SrO) + Co_2O_3$	–	–	"	175
$La_2O_3 + Cr_2O_3 \cdot n\,H_2O$	–	–	"	176
$CaO + TiO_2(Fe_2O_3)$	–	–	amorphous	177
$La_2O_3 + SrO + Ga_2O_3 +$ + MgO (LSGM)	–	–	"	178
$BaPb_xBi_{1-x}O_3$	10	30	monophase	179
$2\,BaO_2 + Bi_2O_3$	5	~50	"	110
$BaO_2 + SrO + Bi_2O_3$	10	~40	"	110
ABO_3 (A = Ca, Sr, Ba, La,Bi; B = Fe, Co, Ni, Mn, Ga, Ti, Mg, Cr, Al, Zr)	20–30	20–40	"	180–185

Depending on the field of application of complex oxides, mechanochemical synthesis can be carried out directly (from oxides or their hydrated forms) or indirectly (from salts including solvents). A large surface area needed for catalytic purposes can be attained in different fashion. However, mechanical treatment of powders containing inert additives, which can either be removed on washing or become constituents of the material, leads to much higher S_s values. Mechanochemical synthesis in the presence of inert solvents that play the role of a matrix (possibly, a liquid solvent matrix at loading) was developed by McCormick *et al.*[186] In essence, the technique is quite similar to soft mechanochemical synthesis.[13] Despite the use of similar (and even the same) terminology the mechanism of synthesis of nanocrystals in the matrix by mechanical treatment of reaction mixtures in solvents[186] is similar to hydrothermal one, being strongly different from direct mechanochemical synthesis in the contact region between solid particles in the reactant mixture.[18]

Mixed-conductivity, $LaCoO_3$-based perovskites for catalytic applications were prepared by mechanochemical synthesis.[97, 170, 171] Grinding in the presence of ZnO-type additives led to unprecedently high specific surface areas of the powders (more than 100 $m^2\ g^{-1}$). Partial replacement of cobalt by copper causes a structural distortion and significant changes in properties.[171] For comparison, a mechanochemically synthesised perovskite $LaCoO_3$ (Ref. 172) had a specific surface area of merely 3.5 $m^2\ g^{-1}$ owing to agglomeration while the specific surface area of $LaMnO_3$ was only 10 $m^2\ g^{-1}$ (Ref. 173). A $LaCrO_3$ perovskite was prepared by mechanochemical synthesis from a mixture of La_2O_3 and amorphous $Cr_2O_3 \cdot n\,H_2O$.[174] The oxide La_2O_3 does not enter in mechanochemical interaction with crystalline Cr_2O_3.[18] Mixing on the atomic level with the hydrated form whose Mohs' hardness is similar to that of La_2O_3 occurs at relatively low intensity of mechanical loading and coalescence occurs upon removal of water.

One of the best oxygen conductors, a LSGM perovskite, was synthesised from an X-ray amorphous precursor by mechanical treatment of a $La_2O_3 + SrO + Ga_2O_3 + MgO$ mixture and subsequent calcination.[177] On sintering until a dense ceramics the grain size was unusually small (250 nm, *cf.* 13 μm for ceramics prepared by traditional technology). According to theory of ultrafast mechanochemical synthesis,[18, 29] the composition of crystallites should be deficient with respect to the harder reactant, MgO, that covers the grains ('core–shell' structure of the nanocomposite) and inhibits their growth on sintering. Moreover, this feature also provides a much higher degradation stability of the ceramics due to the presence of SrO on the grain boundaries.

More than a hundred complex perovskites with high mixed and oxygen conductivities for conducting membranes were prepared.[180–185] Despite a high oxygen deficiency, all perovskites had the cubic symmetry, which was stable until sintering to dense ceramics. Only after high-temperature calcination some systems, *e.g.*, $La_{0.87}MnO_{3-x}$ showed a weak rhombohedral distortion.[180] Mention may be made of a very useful feature of the mechanochemical synthesis of materials for design of asymmetric, selectively permeable multilayered membranes with separated functions. Namely, compatibilisation of materials with allowance for a large number of parameters requires the use of complex compositions including 3 to 6 elements in each cationic sublattice. Complex doping improves

Table 13. Characteristics of perovskite-like compounds of unusual compositions.

Starting mixture [a]	Space group	The unit cell parameters /Å			$E_{1/2}$ /MJ kg^{-1}	Ref.
		a	*b*	*c*		
$BaO_2 + Cu_2O(CuO)$	*P 1* (1)	8.802(8) [b]	6.006(8) [b]	8.420(8) [b]	~15	19, 20, 26
$2\,PbO + Bi_2O_3$	*P 4mm* (99)	3.995(4)	–	5.181(5)	3(1)	26
$2\,PbO + Bi_2O_3$	$P\bar{4}3n$ (218)	4.347(4)	–	–	3.5(1.0)	26
$PbO + Bi_2O_3$	$P\bar{4}3n$ (218)	4.347(4)	–	–	2.3(0.5)	26, 110
$PbO + 2\,Bi_2O_3$	$P\bar{4}3n$ (218)	4.347(4)	–	–	2.3(1.0)	26, 110
$2\,PbO + Tl_2O_3$	–	4.159(4)	–	–	~20	26
$CdO + PbO_2^*$	*P4mm* (99)	4.04(1)	–	4.21(1)	19(5)	26
$HgO + PbO_2^*$	*P2/m* (10)	4.19 [c]	4.28 [c]	4.27 [c]	6(2)	26
$2\,HgO + PbO_2$	$P\bar{4}3m$ (215)	4.080(5)	–	–	2.6(1.0)	26
$HgO + 2\,PbO_2^*$	*P2/m* (10)	4.18 [c]	4.28 [c]	4.27 [c]	8(3)	26
$PbO + CaO + Sb_2O_3$	–	4.725(5)	4.531(5)	3.950(5)	~25	26, 107
$2\,BaBiO_3 + Bi_2O_3$	*Pm3m* (221)	4.368(5)	–	–	~2	26, 107

[a] Activated oxides are asterisked. [b] $\alpha = 84.35(10)^\circ$, $\beta = 89.0(5)^\circ$, $\gamma = 93.7(1)^\circ$; [c] $\beta = 92.8^\circ$

the stability of mechanochemically synthesised perovskites. This approach simplifies rather than complicates the preparation of materials with preset properties. For instance, materials with specified sintering temperatures can be designed,[184] which cannot be done using almost any other method.

Usually, the characteristic times taken to complete room-temperature mechanochemical synthesis are of the order of 20–30 min irrespective of complexity of the composition, oxide melting points, starting dispersion of the oxides and the oxidation state of metals. The only limitation for mechanochemical synthesis is the need of using reactants with Mohs' hardnesses of at most 8. The choice of the optimal procedure for mechanochemical synthesis and the starting reactants with allowance for their hardnesses rather than oxidation state or melting point distinguish the method from other techniques. At the same time researchers abroad use mainly mechanochemical synthesis as 'alternative' method of preparation of known compounds at room temperature. This is not always justified, because often the calcination step is much cheaper than prolonged mechanical treatment.

Usually, perovskites of unusual compositions were unexpected products of mechanochemical synthesis prepared by varying the chemical composition of oxide blends and energy supplied. Such perovskites were detected in multiphase samples in the Pb–Ca–Sb–O system (multiphase character is due to mechanolysis or mechanochemical equilibrium); they are listed in Table 13.

Monophase powders can be prepared from the starting mixtures listed in Table 11 only in a few cases (*e.g.*, $Ba_{2/3}Bi_{1/3}BiO_3$). This is due to similar yields of mechanolysis and synthesis. The perovskite $Ba_{2/3}Bi_{1/3}BiO_3$ (PDF 45-292) with the A and B positions simultaneously occupied by bismuth atoms were first prepared by annealing;[187] the mechanochemically synthesised perovskites $BaBiO_{3-x}$ and $Ba_{2/3}Bi_{1/3}BiO_3$ have cubic symmetry, whereas those grown in equilibrium have a tetragonal symmetry (PDF 40-602, 42-1457).

2. Fluorites and pyrochlores

Like perovskites, fluorites and similar pyrochlores are highly tolerant towards changes in the chemical composition and oxygen deficiency; therefore, the number of fluorite and pyrochlore structures among compounds prepared by mechanochemical synthesis is very large. Fluorite-like Bi_2O_3-based solid solutions are most readily formed.[24, 91, 107, 183, 188] Mechanical treatment of bismuth oxide α-Bi_2O_3 containing typical natural impurities (zinc, lead, antimony, *etc.*) results in the formation of a fluorite-like orthorhombic phase δ'-Bi_2O_3.[91, 107] However, prolonged treatment (~30 min) of high-purity bismuth oxide causes its transformation to the metastable modification β-Bi_2O_3.[188]

High-temperature fluorite-like polymorph δ-Bi_2O_3 possesses a record high oxygen conductivity at temperatures near the melting point, but the conductivity decreases stepwise on cooling. Stabilisation of δ-Bi_2O_3 by doping makes it possible to attain a high conductivity over a wide temperature range and prevent degradation of ceramics due to a change in the volume on cooling. The properties of the materials based on stabilised δ-Bi_2O_3 are extremely attractive for investigations; however, these systems have no practical applications owing to high reactivity towards electrode materials and low stability in reductive media. Nevertheless, monophase nanopowders of the composition $Bi_{1.6}M_{0.4}O_{3-x}$ (M = Ca, $Ca_{0.5}Sr_{0.5}$, In, Y, La) were prepared by mechanochemical synthesis (impurity was detected only in the sample doped with indium having a relatively small ionic radius). In accordance with the theory of ultrafast mechanochemical synthesis[18] a high yield was observed in the mixture with CaO owing to similar hardnesses of the reactants and the effect of the enthalpy of reaction.[188] The results of structural studies carried out assuming a conventional correspondence between the chemical composition of crystallites and the starting mixture are listed in Table 14.

The formation of a fluorite phase with a large unit cell parameter in the sample doped with Sb_2O_3 (1 mol.%) can only be explained by the ultrahigh concentration of vacancies and formation of covalently bonded clusters, as indicated by the very low conductivity. The bismuth atoms are displaced from their positions along the [111] axis. Annealing at temperatures above 600 K causes ordering of these displacements and formation of a stable rhombohedral structure.

Hot pressing of powders at 550 K led to preparation of sufficiently dense samples of metastable nanoceramics.[188] High conductivity was shown by the lanthanum-doped samples with the largest unit cell parameters. A decrease in the lattice symmetry from cubic to rhombohedral on heating was accompanied by an abrupt drop of conductivity.

Complex doping makes the δ-Bi_2O_3-based cubic fluorite structure much more stable. The parameters of the complex fluorites prepared by mechanochemical synthesis and sintered to a dense ceramics are listed in Table 15. It was found that

Table 14. Results of structural studies of fluorites $Bi_{1.6}M_{0.4}O_{3-x}$.[188]

Composition	a /Å	Bi displacement	Distance /Å			M displacement	B(Bi) /Å^2	B(M) /Å^2	B(O) /Å^2	R (%)	D /nm
			Bi−O(1)	Bi−O(3)	Bi−O(3)						
$Bi_{1.6}La_{0.4}O_3$	5.5804(32)	0.036(1)	2.07(1)	2.32	2.55	0	1.0(2)	0.7(2)	3.2(2)	5.67	36
$Bi_{1.6}Y_{0.4}O_3$	5.5116(55)	0.032(1)	2.08(1)	2.28	2.56	0.045(2)	1.0(2)	0.8(2)	3.0(2)	5.34	50
$Bi_{1.6}In_{0.4}O_3$	5.5037(88)	0.032(1)	2.08(1)	2.30	2.51	0.042(2)	0.9(2)	0.9(2)	3.0(2)	5.81	69
$Bi_{1.6}Ca_{0.4}O_{2.8}$	5.5253(24)	0.038(1)	2.04(1)	2.30	2.54	0	0.8(2)	0.8(2)	3.0(2)	5.54	61
$Bi_{1.6}Ca_{0.2}Sr_{0.2}O_{2.8}$	5.5363(29)	0.033(1)	2.08(1)	2.30	2.52	0	0.8(2)	0.6(2)	3.0(2)	5.63	63
$Bi_{1.98}Sb_{0.02}O_3$	5.5484(14)	0.0335(5)	2.08(1)	2.315	2.53	–	0.9(1)	–	3.0(2)	4.42	58

Note. B(Bi), B(M) and B(O) are the thermal factors of the Bi, M and O atoms, respectively.

Table 15. Characteristics of Bi_2O_3-based complex fluorites prepared by mechanochemical synthesis (in numerator) and by sintering (in denominator).[26, 183]

Composition	The unit cell parameter /Å	D /nm	T_s /K
$Bi_{0.5}Ca_{0.1}Y_{0.1}La_{0.1}Ce_{0.1}Gd_{0.1}O_{1.5}$	5.504(9) 5.480(1)	29 320	1373
$Bi_{0.4}Ca_{0.1}Y_{0.1}La_{0.1}Ce_{0.1}Pr_{0.1}In_{0.1}O_{1.5}$	5.466(6) 5.500(1)	34 420	1373
$Bi_{0.4}Ca_{0.1}Y_{0.1}La_{0.1}Ce_{0.1}Gd_{0.1}In_{0.1}O_{1.5}$	5.462(5) 5.479(3)	36 506	1373
$Bi_{0.35}La_{0.4}Ce_{0.25}O_{1.62}$	5.588(3) 5.589(1)	28 1000	1473
$Bi_{0.34}La_{0.33}Ce_{0.33}O_{1.66}$	5.565(2) 5.562(2)	35 730	1573
$Bi_{0.35}Ca_{0.05}Sr_{0.05}La_{0.35}Sm_{0.05}Pr_{0.15}O_{1.52}$	5.601(4) see [a]	52 590	1373
$Bi_{0.3}Ca_{0.03}Sr_{0.06}La_{0.4}Gd_{0.05}Nd_{0.06}Pr_{0.12}O_{1.52}$	5.611(2) see [b]	46 460	1373
$Bi_{0.3}Sr_{0.05}La_{0.4}Ce_{0.15}Gd_{0.05}O_{1.47}$	5.601(3) 5.592(2)	31 460	1473
$Bi_{0.3}La_{0.4}Ce_{0.15}Gd_{0.05}Pr_{0.1}O_{1.5}$	5.591(4) 5.591(1)	35 610	1473
$Bi_{0.3}La_{0.4}Ce_{0.15}Pr_{0.1}Nd_{0.05}O_{1.58}$	5.591(1) 5.585(1)	43 1000	1473

[a] For rhombohedral distortion: parameters are 3.904(1) and 9.870(3).
[b] For rhombohedral distortion: parameters are 3.906(1) and 9.875(3).

there is an optimal value of the unit cell parameter; as the lattice constant exceeds this value, a rhombohedral distortion of the lattice occurs and the conductivity decreases dramatically.

A number of CeO_2-based fluorites were prepared by room-temperature mechanochemical synthesis (*cf.* $T > 2500$ K for melting points of oxides). The high-mixed-conductivity $Ce_{0.7}Pr_{0.3}O_{2-x}$ fluorite seems to be promising as a component of composites for membranes in CMR[182, 183] and compound $Ce_{0.8}Gd_{0.2}O_{1.9}$ is of interest as one of the best ionic conductors for CMR and SOFC applications.[183] Information on the fluorite- and pyrochlore-type compounds prepared by mechanochemical synthesis is summarised in Table 16.

Fluorite structures based on iron-doped CeO_2 and ZrO_2 were synthesised by prolonged mechanical treatment.[191, 192] Stabilised ZrO_2 is formed at a Fe_2O_3 content from 5 mol % to 18.5 mol %,[192] but the fluorite structure remains insufficiently stable from the standpoint of practical applications, because the materials should be sintered at temperatures below 1373 K, which is practically impossible. Interest in iron-doped ceramics based on zirconia is due to unavoidable contamination of abrasive powder when milling using steel balls. Sc^{3+}-Doped nanopowders of complex solid solutions based on ZrO_2 with minimum content of iron impurity ($\sim$0.05 mass % – 0.1 mass %) were prepared[96, 193] by mechanochemical synthesis using a modified correct procedure for mechanical treatment;[49] the concentration of iron in ceramics also decreased owing to sublimation of iron in the course of sintering. Moreover, nanostructuring of powders prepared by mechanochemical synthesis retained due to heavy doping, inhomogeneity inherent in the technique as well as rapid sintering at temperatures below $\sim$1640 K. The dense ceramics showed not only high bending strength ($\sim$190 MPa), but also a high oxygen conductivity at $T < 600$ K. When the samples were annealed or re-heated, the conductivity approached the values typical of conventional ceramics, which can be due to a decrease in the degree of disordering and annealing of vacancies.

Fuentes *et al.*[194–199] reported the preparation of solid solutions with the pyrochlore structure by mechanochemical synthesis. The evolution of the structure and morphology of the mechanochemically synthesised, highly disordered pyrochlores after annealing was studied by powder X-ray diffraction and Raman spectroscopy. A full-profile Rietveld analysis of the X-ray diffraction patterns revealed a disorder typical of mechanochemically synthesised complex oxides, namely, mixed occupation of the positions 16*c* and 16*d* gradually approaches the equilibrium values as the temperature increases, but no 100% ordering is attained (Table 17). An *a priori* analysis was carried out assuming that the crystallites and starting mixture have the same composition (contamination with 2% – 4% of ZrO_2, reduction of oxides and different chemical compositions of the crystallites and disordered amorphous phase were ignored). Since in this case the reactants have slightly different hardnesses (no reference data on the Mohs' hardnesses of rare-earth element oxides are available), there are no grounds to expect a large difference between the chemical compositions of crystallites and starting mixture. For other mechanochemically synthesised pyrochlores characterised by the reactant hardness difference from $\sim$0.5 to 1.5, the best *R*-factor was attained with allowance for disordering and deficiency of the hard reactant,[189] *e.g.*, $(Hg_{1.8}Sb_{0.16}).(Hg_{0.2}Sb_{1.8})OO_{5.9}$.

Contrary to other titanates, the characteristic feature of $Gd_2Ti_2O_7$ is a weak disordering in the A-sublattice, which is due to differences in the ionic radii (1.0, 0.97 and 0.96 Å for heptacoordinate Gd^{3+}, Dy^{3+} and Y^{3+}, respectively, *cf.* only 0.61 Å for Ti^{4+} in an octahedron). The pyrochlore structures of solid solutions $Dy_2(Ti_{1-y}Zr_y)_2O_7$ and $Gd_2(Sn_{1-y}Zr_y)_2O_7$ ($0 \leqslant y \leqslant 1$) were obtained after treatment with ceramic balls

Table 16. Characteristics of compounds with fluorite (F) and pyrochlore (P) structures prepared by mechanochemical synthesis.

Starting mixture composition	Structure	a /Å	Time /h	$E_{1/2}$ /MJ kg^{-1}	Ref.	Starting mixture composition	Structure	a /Å	Time /h	$E_{1/2}$ /MJ kg^{-1}	Ref.
$3\,Bi_2O_3 + 2\,Sm_2O_3$	F	5.515	6		24	$3\,Bi_2O_3 + 0.6\,Y_2O_3 + + 0.4\,Sm_2O_3$	F	5.500(5)	0.25	> 10	91
$3\,Bi_2O_3 + 2\,Y_2O_3$	F	5.4691	6		24						
$3\,Bi_2O_3 + Y_2O_3 + Sm_2O_3$	F	5.4892	6		24	$2\,CaO + Sb_2O_3 + + 0.05\,La_2O_3$	F	5.377(5)	0.25	> 10	190
$CeO_2 + 2\,Sm_2O_3$	F	5.4386	6		24						
$0.7\,CeO_2 + 0.15\,Bi_2O_3$	F	5.4209	6		24	$3\,Bi_2O_3 + 2\,HgO + Tl_2O_3$	F		0.25	~ 35	162
$7\,CeO_2 + PrO_{1+x}$	F		0.3		183	$4\,Bi_2O_3 + Tl_2O_3$	F		0.25	~ 35	162
$8\,CeO_2 + Gd_2O_3$	F		0.3		182	$Tl_2O_3 + 4\,PbO_2$	P		0.25	3.3(6)	162
$2\,CdO + Sb_2O_3$	F	5.150(6)	0.25	~ 20	189	$CeO_2 + ZrO_2 + Fe_2O_3$	F		> 10		191,
$2\,PbO + Sb_2O_3$	F	5.520(6)	0.25	2.5(3)	95						192
$2\,HgO + Sb_2O_3$	F	5.153 (5)	0.25	3.2(3)	189	$ZrO_2 + Sc_2O_3 + CeO_2$	see [a]		0.5		96,
$2\,CdO + Sb_2O_5$	P	10.254(8)	0.25	4.0(3)	189						193
$2\,PbO + Sb_2O_5$	P	10.440(8)	0.25	4.5(3)	95	$Gd_2O_3(Dy_2O_3) + TiO_2$	P	10.212, 10.147	20		194
$2\,HgO + Sb_2O_5$	P	10.325(8)	0.25	3.5(3)	189						
$2\,CdO + Nb_2O_5^*$	P	10.33(1)	0.25	11(3)	26	$Ln_2O_3(Y,Gd,Dy) + TiO_2$	P	10.161, 10,212, 10.147	19		195
$2\,PbO + Nb_2O_5^*$	P	10.66(1)	0.3	31(6)	135						
$2\,HgO + Nb_2O_5^*$	P	10.45(1)	0.3	8(2)	26						
$2\,PbO + Ta_2O_5^*$	P	10.647(8)	0.5	30(6)	26	$Dy_2O_3 + TiO_2(ZrO_2)$	P	10.1366 – 10.4541	19		196
$2\,HgO + Nb_2O_5^*$	P	10.466(8)	0.3	19(5)	26						
$3\,Bi_2O_3 + VO_2$	F	5.550(3)	0.25	> 10	82	$Gd_2O_3 + SnO_2(ZrO_2)$	P	10.471 – 10.524	18		197
$2\,Bi_2O_4 + V_2O_3$	F	5.506(3)	0.25	~ 5	82						
$Bi_2O_3 + 2\,Sb_2O_3$	F	5.551(4)	0.25	2.1(4)	107	$Gd_2O_3 + TiO_2(ZrO_2)$	F		19		198,
$3\,Bi_2O_3 + Sb_2O_3$	F	5.455(3)	0.25	1.8(3)	107						199
$2\,Sb_2O_3 + CaO$	F	5.451(4)	0.25	13(6)	107	$Y_2O_3 + TiO_2(ZrO_2)$	P		19		199
$0.72\,Sb_2O_3 + 0.08\,Bi_2O_3 + + 0.4\,CaO$	F	5.360(5)	0.25	12(5)	107	$0.82\,ZrO_2 + 0.09\,La_2O_3$	see [a]	6			200

[a] Amorphous sample + F.

Table 17. Changes in structural parameters of pyrochlores prepared by mechanochemical synthesis after annealing for 12 h at different temperatures.[197]

Parameters	Mechanochemical synthesis	Annealing at temperature /K		
		923	1073	1473
$Y_2Ti_2O_7$				
a /Å	10.161(1)	10.1281(5)	10.1095(2)	10.1004(1)
Y : Ti (see [a])	0.72 : 1.28	1.10 : 0.90	1.75 : 0.25	1.93 : 0.07
Y : Ti (see [b])	1.28 : 0.72	0.90 : 1.10	0.25 : 1.75	0.07 : 1.93
D_{iso} /nm (see [c])	5.3	8.3	12.9	133.3
$Gd_2Ti_2O_7$				
a /Å	10.212(1)	10.2038(8)	10.2025(2)	10.2002(1)
Gd : Ti (see [a])	1.84 : 0.16	1.87 : 0.13	1.893 : 0.107	1.881 : 0.119
Gd : Ti (see [b])	0.16 : 1.84	0.13 : 1.87	0.107 : 1.893	0.119 : 1.881
D_{iso} /nm (see [c])	9.6	16.8	14.7	190.5
$Dy_2Ti_2O_7$				
a /Å	10.147(2)	10.150(3)	10.1412(2)	10.1333(1)
Dy : Ti (see [a])	0.63 : 1.37	1.63 : 0.37	1.817 : 0.183	1.881 : 0.119
Dy : Ti (see [b])	1.37 : 0.63	0.37 : 1.63	0.183 : 1.817	0.119 : 1.881
D_{iso} /nm (see [c])	6.7	10.5	12.5	53.3

[a] 16*c* (0 0 0). [b] 16*d* (1/2 1/2 1/2). [c] Isotropic crystallite size.

(stabilised ZrO_2 ceramics) for 19 h.[196, 197] The formation of a fluorite structure of the solid solution based on ZrO_2 doped with 18% La_2O_3 after mechanical treatment for 6 h was reported.[200] Heating to 1273 K was followed by the formation of an ordered pyrochlore $La_2Zr_2O_7$ and isolation of excess ZrO_2. These pyrochlores were studied in the framework of a search for new solid electrolytes; however, it should be noted that fluorite-like disordered solid solutions have a higher conductivity.

Mechanochemical synthesis of fluorites from salts in a dilute media was reported.[201] It was found that the unit cell parameters of the fluorite structures of the same chemical composition $4\,CeO_2 + Sm_2O_3$ prepared by different methods were strongly different, namely, 5.4386 Å (mechanochemical synthesis from oxides),[24] 5.450 Å (thermal synthesis) and 5.4530 Å (mechanochemical synthesis in dilute media followed by removal of salts and calcination).[186] These differences were ascribed to inhomogeneity of the solid solution prepared by mechanochemical synthesis from oxides and to high concentration of vacancies.

A large number of compounds whose characteristics are listed in Table 16 are of no concern to practice. However, phenomena revealed in studies of some systems are of interest to materials science. For instance, the fluorite $Cd_2Sb_2O_5$ is oxidised while the pyrochlore $Cd_2Sb_2O_7$ is reduced on heating in air. As identical compositions described by the chemical formula $Cd_2Sb_2O_6$ are attained, the processes do not stop. Rather, each of them continues to drive its way, *i.e.*, the fluorite is transformed to pyrochlore on oxidation, whereas pyrochlore is almost transformed to fluorite on reduction (!).[189] The dependence of lattice constant of the fluorite phase formed in the system $Bi_2O_3 - Sb_2O_3$ on the average ionic radius is opposite to that predicted by Vegard. These metastable fluorites are black and similar to dielectrics in conductivity. On soft annealing (~ 700 K) the samples turn yellow, but the lattice constant still remains too large.[107] Unusual properties of these fluorites manifest themselves in the IR and Raman spectra. The pyrochlore $Hg_2Sb_2O_7$ readily undergoes reduction with the loss of mercury on heating to 673 K.[189] The remaining low-

density product undergoes transformation to another structure, which is similar to pyrochlore and comprises triangular clusters $(Hg_3)^{4+}$ observed previously only in three systems.[202] Some phases prepared by mechanochemical synthesis show complete disappearance of Raman scattering after annealing in a narrow temperature range.[110]

Fluorite-like structures with doubled tetragonal unit cell were prepared by mechanochemical synthesis of mixtures $2\,Bi_2O_3 + VO_2$ and $Bi_2O_4 + VO_2$.[82] The formation of pyrochlores was also observed in numerous studies on the synthesis of piezoelectric materials with the perovskite structure.

3. Sillenites

Powders of compounds with the structure of sillenite $Bi_{12}SiO_{20}$ are of no interest to practice; high-purity single crystals are mainly used. However, this structural type is very important for mechanochemical studies aimed at comprehensive understanding of the unique phenomenon of ultrafast mechanochemical synthesis of complex oxides. Given a cubic lattice symmetry, the X-ray diffraction patterns exhibit a large number of reflections. Moreover, broadening of reflections from nanopowders prepared by mechanochemical synthesis is minimum: the size of crystallites reaches 90 – 100 nm. For this structural type the ratio of the number of peaks observed to the number of parameters varied is maximum and corresponds to conventional situation in X-ray studies of powder samples. This structural type was first revealed in studies of mechanochemical reactions in the system $PbO - Bi_2O_3$.[203–205] Cations with ionic radii similar to that of bismuth and suitable for occurrence of this structural type were considered in a study.[162] Sillenites prepared by mechanochemical synthesis can be divided into two groups: (1) compounds described by the chemical formula $Bi_{12}MO_{20-x}$ (partial occupation of the 2*a* site by bismuth) and (2) compounds in which a large proportion of Bi atoms in the 24*f* position is replaced by other atoms. The first group comprises compounds with M = V;[82] Ge;[108] Cd and Tl;[162] and Zn, Si, Pb^{4+} and Fe.[205] The second group is of greater interest, because it allows one to go far beyond the traditional structural model for sillenites.[206, 207] The characteristics of metastable sillenites (secondary products of mechanochemical synthesis) are presented in Table 18.

Table 18. Atomic positions and thermal factors of sillenites of nominal composition Bi_2PbO_4, Bi_4HgO_7, $Bi_{12}Cd_{0.7}O_{18.7}$ prepared by mechanochemical synthesis (after annealing at T = 773 K), R = 8.36%, 9.28% and 9.1%, respectively.[162]

Atom	Position	Position coordinates			Occupation	B/Å^2
		x	y	z		
Bi(Pb)	24*f*	0.181(1)	0.323(1)	0.025(1)	1	0.6(1)
Bi(Hg)		0.182(1)	0.315(1)	0.017(1)	1	0.6(1)
Bi		0.182(1)	0.315(1)	0.010(1)	1	0.6(1)
Bi	8*c*	0.017(1)	0.017(1)	0.017(1)	0.14(1)	0.3(1)
Bi	8*c*	0.017(1)	0.017(1)	0.017(1)	0.20(1)	0.3(1)
Cd	2*a*	0	0	0	0.70(5)	0.3(1)
O(1)	24*f*	0.125(5)	0.25(1)	0.50(1)	0.9167	1.0(5)
		0.128(5)	0.27(1)	0.50(1)	0.96	1.0(5)
		0.128(5)	0.267(5)	0.50(1)	1	1.0(5)
O(2)	8*c*	0.190(5)	0.190(5)	0.190(5)	1	1.0(5)
		0.190(5)	0.190(5)	0.190(5)	1	1.0(5)
		0.190(5)	0.190(5)	0.190(5)	1	1.0(5)
O(3)	8*c*	0.117(10)	0.117(10)	0.117(10)	0.42(3)	2.0(5)
		0.117(10)	0.117(10)	0.117(10)	0.60(3)	2.0(5)
		0.210(10)	0.210(10)	0.210(10)	0.7(3)	2.0(5)

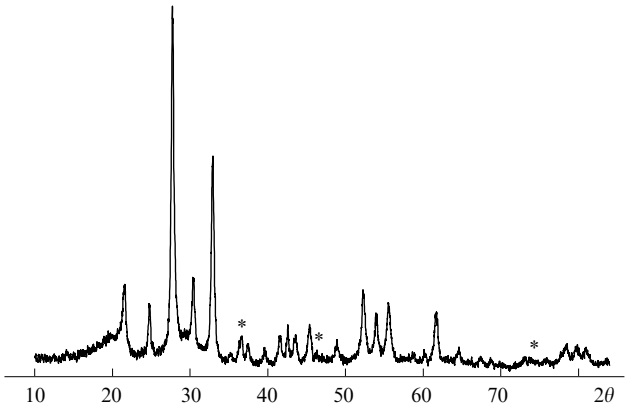


Figure 14. X-Ray diffraction pattern (Cu K_α radiation) of Bi_2CoO_4 sollenite (E_s = 30 MJ kg^{-1}) prepared by mechanochemical synthesis. Extra peaks of the superlattice of incommensurate phase are asterisked.

The Pb^{2+} and Hg^{+} ions are in some sense electronic analogues to Bi^{3+} having a lone electron pair; therefore, it is not surprising that they replace bismuth in the sillenite lattice. When no small cations are available, the 2*a* position is partially occupied by bismuth atoms with a minor displacement along the [111] axis, *i.e.*, the coordination of Bi^{3+} can be represented as an umbrella with a coordination number of 3 (similar coordination occurs in fluorites with high oxygen deficiency), the 2*a* site is transformed into the 8*c* site (see Table 16).

However, the known sillenite phases include a number of unusual solid solutions in the system $Bi_2O_3 - CoO$ up to a compound of composition $Bi_{10}Co_{14}Co_2O_{40}$ (PDF 39-1010).[208] Mechanical treatment of a mixture of oxides $Bi_2O_3 + CoO$ led to formation of a Bi_2CoO_4 sillenite (Fig. 14)[26] with the lattice constant a = 10.217(2) Å very similar to that of the known phase $(Bi_{16.32}Co_{6.96})Co_{1.94}O_{40}$ (PDF 82-1323, a = 10.199 Å). An interesting feature of this sillenite consists in the extra peaks in the X-ray diffraction patterns; these can be attributed to

Table 19. Interplanar spacing (d) in structure of metastable sillenites and possible indexation of observed extra peaks on annealing in incommensurate superlattice ($2a \cdot 2a \cdot 2a$) model.[162]

d_{obs}/Å	h k l	d_{calc}/Å	d_{obs}/Å	h k l	d_{calc}/Å
Sample Bi_4PbO_7 (913 K) or Bi_2PbO_4 (913K) a = 10.262(6) Å, $1/2\,a^*$ = 10.255(8) Å			Sample Bi_4CdO_7 (813 K), a = 10.194(4) Å, $1/2\,a^*$ = 10.227(13) Å		
6.487	3 1 0	6.487	3.449	5 3 1	3.457
2.347	6 6 2	2.347	3.307	6 1 1	3.318
2.154	9 3 1	2.154	3.191	5 4 1	3.194
1.957	10 3 1	1.957	2.629	6 5 0	2.619
1.728	11 4 2	1.727	2.557	8 0 0	2.557
1.607	9 9 1	1.607	2.504	7 3 3	2.500
1.358	14 4 4	1.358	2.348	6 6 2	2.346
Sample Bi_4HgO_7 (573 K), a = 10.209(6) Å, $1/2\,a^*$ = 10.334(15) Å			2.244	9 1 1	2.245
			2.126	8 5 2	2.121
			1.949	10 3 1	1.950
4.882	3 3 0	4.886	1.908	9 5 3	1.907
2.514	8 2 0	2.514	1.834	10 5 0	1.830
2.139	9 3 2	2.138	1.724	11 4 2	1.723
1.933	9 5 3	1.933	1.589	11 6 3	1.588
1.813	9 7 1	1.811	1.484	10 9 3	1.484
1.618	10 8 0	1.618	1.146	14 11 1	1.147

reflections of the incommensurate superlattice $1/2\,a^* = 10.171(10)$ Å, because the reflections of the types $(h^2+k^2+l^2) \neq 17, 23, 63$ are impossible or forbidden for the sillenite space group $I23$ (197). Many extra peaks are observed in the X-ray diffraction patterns of metastable sillenites Bi_4PbO_7, Bi_2PbO_4, Bi_4HgO_7 and a sillenite [162] formed in the decomposition of the body-centred phase Bi_4CdO_7 on annealing (Table 19); they were also attributed to incommensurate phases with the superlattice.

4. Spinels

Spinels consist of light and moderately heavy elements; therefore, the mechanochemical yield should also be relatively low. Attempts to prepare crystalline products by prolonged mechanochemical synthesis should lead to reduction of oxides and going beyond the tolerance limits of this structural type; this indeed was observed in the experiments.[209] The experimental results on mechanochemical synthesis of spinels are in accordance with theory of ultrafast mechanochemical synthesis of complex oxides;[18] they are listed in Table 20.

Table 20. Characteristics of spinels prepared by mechanochemical synthesis.

Starting mixture	Treatment duration /h	Crystallite size /nm	Composition from X-ray diffraction data	Ref.
$ZnO + Fe_2O_3$	600	~5	multiphase	210
	0.25	~30	"	20
	3	~10	monophase	211
	12–36		"	212–215
		15	multiphase	215
$NiO + ZnO + Fe_3O_4$		~10–50	monophase	216
$NiO + Fe_2O_3$	50	6	"	23
		9	"	217
$CoO + Fe_2O_3$	15	12	monophase from amorphous precursors	218
$4\,CoO + Fe_2O_3$	15	12	multiphase from amorphous precursors	218
$MgO + Fe_2O_3$	12	5–15	monophase	219–221
$MnO(ZnO) + Fe_2O_3$	1		amorphous	222
$Li_2CO_3 + 4\,MnO_2$	0.17		multiphase	223–224
$4\,LiOH + 5\,MnO_2$	2		amorphous	225

Traces of a spinel (~20% of the total intensity of the X-ray diffraction peaks of this phase in the mixture) were first detected when milling a mixture of oxides $ZnO + Fe_2O_3$ for 600 h.[210] Mechanochemical synthesis in an AGO-2 mill takes 10–15 min to complete ($E_{1/2} \sim 8$ MJ kg^{-1}); however, due to hardness difference between hematite ($MH = 6$) and zincite ($MH = 5$) the secondary product with the spinel structure is iron deficient.[20,26] Powder X-ray diffraction detected traces of hematite (~17% of the initial content); this value varied slightly upon doubling the amount of energy supplied. Analysis of the peak intensities revealed the best R-factor for the model of formation of a disordered, iron-deficient spinel.[20] In other studies the residual hematite was also detected during prolonged mechanical treatment and then disappeared due to amorphisation and gradual reaction with the spinel. The starting reactants used for mechanochemical synthesis of magnesium ferrite have the same hardness; therefore, the residual hematite is not detected by powder X-ray diffraction [220] despite the lower mechanochemical yield owing to low molecular masses of the reactants. Prolonged mechanical treatment causes amorphisation of spinels,[209,218,226] which can only be explained by reduction. An attempt to prepare a spinel of composition Co_2FeO_{4-x} by mechanical treatment of amorphous precursor failed, because the product decomposed with the formation of metallic cobalt.[218]

The preparation of Ni-ferrite was reported.[23] However, a pure spinel is only formed on annealing at a low (compared to conventional synthesis) temperature of about 1273 K. Mechanochemical synthesis of this spinel was reproduced on a more powerful AGO-2 mill and a spinel with a crystallite size of ~10 nm was prepared.[26] However, the yield was very low ($E_{1/2} > 50$ MJ kg^{-1}) owing to the insignificant role of the enthalpy of the chemical reaction and low molecular masses of the reactants. Taking into account the threshold character of mechanochemical synthesis and very broad peaks from the product in the X-ray diffraction pattern, one can suggest that the authors of study [23] took the residual starting reactant (partially reduced iron oxide) for spinel. A similar situation was also reported in the case of cuprospinel $CuFe_2O_4$. A $CuO + Fe_2O_3$ mixture was subjected to prolonged mechanical treatment and the magnetisation of nanoparticles formed was studied.[227] It was found to be four times lower than that expected for cuprospinel. A revision study of mechanochemical synthesis of cuprospinel $CuFe_2O_4$ in an AGO-2 mill showed that the mechanochemical yield is very low, $E_{1/2} > 50$ MJ kg^{-1} (Ref. 26). In the reduction of oxides (especially, CuO) the X-ray diffraction patterns of Cu_2O and hypothetical product of mechanochemical synthesis ($CuFe_2O_4$) are almost indistinguishable due to the broadening of the X-ray reflections from the nanostructured nanopowders. Based on the appearance of a new broadened peak in the X-ray diffraction pattern of a mixture $LiOH + CoOOH$, it was concluded that a low-temperature modification of spinel $LiCoO_2$ was prepared by mechanochemical synthesis.[228] However, the reactant hardnesses differ appreciably and a large contribution of enthalpy in the case of hydrated compounds should not be expected. The molecular masses of the reactants are low; therefore, the mechanochemical yield should be very low. Using the available X-ray diffraction patterns,[223,224] it is impossible to distinguish between the peaks of the hypothetical product of mechanochemical synthesis (starting mixture $LiCO_3 + 4\,MnO_2$, see Table 20) and the Mn_2O_3 peaks (owing to small contribution of lithium to intensity), which is expected to appear with the specified duration of mechanical treatment (energy, E_s, supplied during 10 min was estimated at 50 MJ kg^{-1}).

The aforesaid shows that analysis of complicated situations, where the main method (powder X-ray diffraction) is little informative due to amorphisation of products, should be carried out taking into account the mechanism of mechanochemical synthesis.

5. Structures with body-centred and face-centred cubic lattices

Most metallic alloys have body-centred and face-centred cubic lattices (BCC- and FCC-structures, respectively). Among complex oxides, the number of the BCC- and FCC-phases is small. A product with the BCC-structure prepared [107] by mechanochemical synthesis from the starting mixture $2\,CaO + Bi_2O_3$ [$a = 4.240(3)$ Å, $E_{1/2} = 8(3)$ MJ kg^{-1}] is similar to the known phase $Bi_{1.09}Ca_{0.91}O_{2.55}$ (PDF 40-0314). A

BCC-phase formed upon mechanical treatment of a mixture $CdO + 2\,Bi_2O_3$ [$a = 4.282(3)$ Å, $E_{1/2} = 16(4)$ MJ kg^{-1}] [162] with the parameters of the known phase of the same composition prepared by quenching of a melt of these oxides ($a = 4.2818$ Å, PDF 41-544). Prolonged mechanical treatment of a mixture $2\,HgO + Bi_2O_3$ caused reduction of the oxides and formation of a new phase $Hg_2Bi_2O_4$ [$E_{1/2} = 18(6)$ MJ kg^{-1}] with monoclinic lattice symmetry ($a = 8.04$, $b = 4.52$, $c = 6.9$ Å, $\beta = 99.7^\circ$); this phase can be treated as a distorted BCC-structure.[26]

A few compounds with the FCC-structure $LiMO_2$ (M = Ti, Mn, Fe) were prepared by mechanical treatment of oxides and metals.[229] Compound $LiMnO_2$ is characterised by weak ordering of cations, whereas $LiCoO_2$ and $LiNiO_2$ have a completely disordered rock salt structure.

A perovskite was prepared [230] by the reaction

$$2\,CaO + Fe_2O_3 \longrightarrow Ca_2Fe_2O_5\,.$$

However, the theory of ultrafast mechanochemical synthesis of complex oxides [18] predicts that for this mixture of reactants (Mohs' hardness of CaO and Fe_2O_3 is ~ 4 and 6, respectively) the primary product should be similar in composition to $\sim 3\,CaO \cdot Fe_2O_3$. No structures corresponding to this chemical composition are known; therefore, powder X-ray diffraction can detect only the secondary products formed in the reaction

$$3\,CaO \cdot Fe_2O^*_{3-x} + Fe_2O^*_{3-x} \longrightarrow \sim Ca_5Fe_6O^*_{16-x}\,.$$

The formation of a perovskite is hardly probable owing to high inhomogeneity and oxygen deficiency, which increases as the treatment durtation increases. Moreover, a fraction of calcium oxide leaves the reaction owing to irreversible hydration and carbonisation (dynamics of this process is governed by the mechanical treatment procedure and subsequent operations with powders). A revision study [26] of mechanochemical synthesis in this system showed that mechanical treatment of the mixture of oxides leads to formation of a new tetragonal phase with the structural motiff of partially ordered solid solution of iron oxide in CaO [$a = 6.793(2)$ Å $\sim \sqrt{2}a^*$, $c = 9.618(2)$ Å $\sim 2a^*$, space group $P4_22_12$ (94), where a^* is the lattice constant of the rock salt structure similar to the structure of the known phase $CaFeO_2$, $a = 4.762$ Å, PDF 21-917]. High concentration of structural vacancies causes a very fast degradation of the product in air owing to reactions with water vapours and CO_2 resulting in the phases showing narrow peaks of portlandite $Ca(OH)_2$ and calcite $CaCO_3$, which can also be seen in the X-ray diffraction patterns reported in Ref. 230.

6. Layered complex oxides

According to the mechanism of mechanochemical synthesis, the product is formed under quenching on unloading. The formation of ordered layered structures under these conditions can be treated as an exception rather than a rule. For instance, all attempts to prepare, for instance, a layered perovskite $YBa_2Cu_3O_{7-x}$ have failed. Moreover, mechanical treatment of this oxide is followed by almost irreversible formation of a tetragonal and then cubic lattice without manifestation of high-temperature superconductivity (HTSC).[30, 226] The authors of communications on mechanochemical synthesis of layered HTSC phases do not actually use correct terms.[30] Nevertheless, the simplest representatives of layered complex oxides were prepared by mechanochemical synthesis.

The first synthesis of a layered complex oxide Cd_2PbO_4 was carried out by mechanical treatment of a mixture $CdO + PbO_2$.[26, 203, 204] The Mohs' hardness of the reactants is 3 and 5, respectively; therefore, in accordance with the theory of ultrafast mechanochemical synthesis of complex oxides [18] the primary product should be similar in composition to Cd_2PbO_4. Indeed, the mechanochemical yield of this phase was sufficiently high. One could expect the formation of $CdPbO_3$ as the secondary product. However, the dynamics of the Pb^{4+} reduction in the course of mechanical treatment is rather fast and, as a consequence, the structural type of the product remained unchanged in the secondary loading events

$$Cd_2PbO^*_4 + PbO^*_{2-x} \longrightarrow (Cd_{3/2}Pb_{1/2})PbO_4\,.$$

The use of mechanically pre-activated lead dioxide as the starting reactant led [203, 204] to formation of another (cubic) phase with the structural type of bixbyite Mn_2O_3

$$CdO + PbO^*_2 \longrightarrow CdPbO_3\,.$$

On prolonged mechanical treatment the cubic $CdPbO_3$ transformed to the hexagonal polymorph. Figure 15 presents the structural motiff of the Cd_2PbO_4 phase (only the heavy atoms are shown). Phases belonging to the Cd_2PbO_4 structural type were prepared by mechanochemical synthesis from the starting mixtures $CdO + 2\,PbO_2$, $HgO + PbO_2$, $HgO + 2\,PbO_2$, $2\,PbO + Tl_2O_3$, $Tl_2O_3 + 4\,PbO_2$ and $PbO + 2\,Sm_2O_3$.[26, 162] High tolerance of this structural type is proved by its observation [162] upon mechanical treatment of a complex mixture of oxides $CdO + HgO + PbO + Tl_2O_3 + PbO_2$.

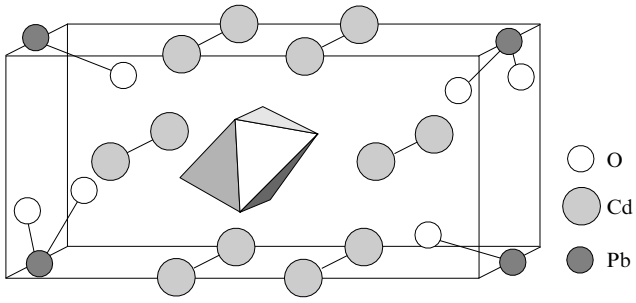


Figure 15. Layered structure of the Cd_2PbO_4 type.

A layered perovskite (K_2NiF_4 structural type) was mechanochemically synthesised from a mixtures of simple oxides $2\,HgO + PbO_2$ [space group $I4/mmm$ (139), $a = 4.1$, $c = 12.2$ Å, $E_{1/2} = 3(1)$ MJ kg^{-1}, primary product] and $HgO + PbO_2$ ($a = 4.138$, $c = 13.35$ Å, secondary product).[26, 203, 204] The Sr_2TiO_4 phase (simplest representative of a family of the Ruddlesden–Popper phases) was detected [31] in the form of individual crystallites as the secondary product by HREM. The formation of a layered phase in the similar system $2\,BaO_2 + TiO_2$ was also detected [93] by electron diffraction on individual particles, but the X-ray diffraction patterns were little informative, being similar to those obtained from amorphous substances. The situation in this system was complicated by the occurrence of mechanochemical equilibrium, namely, the content of the Ba_2TiO_4 phase was low in the initial stage (powder X-ray diffraction data), then increased and reached a maximum value after mechanical treatment for ~ 100 h; eventually, this phase disappeared upon treatment for even longer time. Only one crystalline product, perovskite $BaTiO_3$,

was detected after treatment for 460 h. The formation, with very high mechanochemical yield ($E_{1/2} = 2.5$ and 3.5 MJ kg^{-1}), of new phases assigned to the K_2NiF_4 structural type was unexpectedly detected [162] in the systems $PbO + 2\,La_2O_3$ and $HgO + La_2O_3$. Layered perovskites of complex composition and high mixed conductivity for selective membranes were prepared [231] after mechanical treatment in an AGO-2 mill for 25 min.

Layered Aurivillius phases belonging to the BIMEVOX family possess record high oxygen conductivity at moderate temperatures and some other interesting properties. Therefore, attempts to prepare these phases by mechanochemical synthesis were undertaken repeatedly,[84, 226, 232–234] but all of them have failed. Treatment of an oxide mixture $2\,Bi_2O_3 + V_2O_5$ in an AGO-2 mill gave an amorphous mixture owing to high contamination, inhomogeneity and reduction.[90, 97] Milling over a period of seven days only led [233, 234] to amorphous mixture due to low intensity of mechanical loading. It was reported [29] that only compounds with a congruent character of melting can be prepared by mechanochemical synthesis; however, the $Bi_2VO_{5.5}$ phase shows incongruent melting. Two Aurivillius phases, Bi_2VO_5 and Bi_2GeO_5, in the form of monophase powders were prepared by mechanochemical synthesis in the systems $Bi_2O_3 - VO_2$ (see Refs 82, 108, 235 and 236) and $Bi_2O_3 - GeO_2$.[108] The Bi_2VO_5 phase was detected [82, 108, 235] as the secondary product upon mechanical treatment of a mixture of composition $2\,Bi_2O_3 + V_2O_5$ (owing to partial reduction).

Monophase powders ($E_s = 60$ MJ kg^{-1}) were prepared by mechanochemical synthesis using mixtures $Bi_2O_3 + VO_2$ (samples I in Table 21), $2\,Bi_2O_3 + 0.2\,ZnO + 0.9\,V_2O_5$ (samples II), $2\,Bi_2O_3 + 0.1\,M_2O_3 + 0.9\,V_2O_5$ (M = Sc, Sb, In; samples III – V, respectively) and $1.6\,Bi_2O_3 + 0.4\,PbO + V_2O_5$ (samples VI). Structural studies showed that, similarly to other compounds prepared by mechanochemical synthesis, the Aurivillius phases belonging to the BIMEVOX family have disordered structures, namely, a fraction of bismuth atoms occupies the vanadium sites, thus making their own lattice sites vacant; in turn, partial occupation of these vacancies by relatively large cations (*e.g.*, In^{3+} and Sb^{3+}) is possible.

It should be noted that, in addition to high disordering, which violates the layered character of the structure, the starting powders are characterised by high concentrations of structural vacancies that decrease by about 1.5 times upon sintering to dense ceramics. The conductivity of the best BIMEVOX ceramics sintered from nanopowders prepared by mechanochemical synthesis [236] is very similar to the record conductivity attained in ceramics with homogeneous chemical composition and ordered structure.

Table 21. Structural parameters and content of structural vacancies (f) in BIMEVOX compounds prepared by mechanochemical synthesis and after annealing at 1000 K.[235]

Sample	a/Å	c/Å	V/Å^3	f	Structural formula
I	3.934(2)	15.475(8)	239.50	0.247	$Bi_{1.54}(V_{0.85}Bi_{0.15})O_{4.24}$
I_{anneal}	3.940(1)	15.380(3)	238.75	0.164	$Bi_{1.65}(V_{0.89}Bi_{0.11})O_{4.87}$
II	3.925	15.415	237.48	0.200	$Bi_{1.59}(V_{0.77}Bi_{0.14}Zn_{0.09})O_{4.61}$
II_{anneal}	3.924	15.415	237.36	0.145	$Bi_{1.77}(V_{0.83}Bi_{0.08}Zn_{0.09})O_{4.93}$
III	3.940	15.398	239.03	0.209	$Bi_{1.54}(V_{0.76}Bi_{0.15}Sc_{0.09})O_{4.58}$
III_{anneal}	3.929	15.458	238.63	0.155	$Bi_{1.72}(V_{0.82}Bi_{0.09}Sc_{0.09})O_{4.89}$
IV	3.921	15.499	238.29	0.178	$Bi_{1.62}Sb_{0.02}\,.\,.(V_{0.79}Bi_{0.14}Sb_{0.07})O_{4.76}$
IV_{anneal}	3.928	15.465	238.61	0.132	$Bi_{1.79}Sb_{0.01}\,.\,.(V_{0.84}Bi_{0.08}Sb_{0.08})O_{5.02}$
V	3.928	15.355	236.92	0.187	$Bi_{1.6}In_{0.02}\,.\,.(V_{0.78}Bi_{0.15}In_{0.07})O_{4.7}$
V_{anneal}	3.931	15.472	239.09	0.136	$Bi_{1.78}In_{0.01}\,.\,.(V_{0.84}Bi_{0.08}In_{0.08})O_{5.0}$
VI	3.932	15.420	238.40	0.188	$Bi_{1.45}Pb_{0.16}(V_{0.87}Bi_{0.13})O_{4.7}$
VI_{anneal}	3.9315	15.399	238.02	0.152	$Bi_{1.64}Pb_{0.09}(V_{0.91}Bi_{0.09})O_{4.91}$

Bismuth titanate $Bi_4Ti_3O_{12}$ having a layered perovskite structure possesses good ferroelectric properties, this being a subject of intensive research. Kong *et al.*[237] were the first who reported the preparation of this phase in the form of almost monophase nanopowders by mechanochemical synthesis after milling of a mixture of the bismuth and titanium oxides for 15 h. However, the unit cell parameters of this layered phase ($a = 5.449$, $b = 32.815$ and $c = 5.41$ Å, PDF 35-795) are too large to characterise the phase prepared by mechanochemical synthesis. Indeed, analysis of X-ray diffraction patterns carried out in a revision study [26] involving mechanical treatment of a corresponding mixture of oxides in an AGO-2 mill up to $E_s = 33$ MJ kg^{-1} revealed no formation of the layered crystalline phase; only a gradual formation of a broad halo characteristic of amorphous state was observed. Similar results were obtained in the studies [226, 238] whose authors attained the amorphous state by mechanical treatment of simple oxides and a layered complex oxide $Bi_4Ti_3O_{12}$ obtained by solid-phase synthesis.

Ceramics with good parameters was sintered [239] from an amorphous precursor prepared by mechanical activation of a $2\,Bi_2O_3 + 3\,TiO_2$ mixture. However, the X-ray diffraction patterns of the samples $2\,Bi_2O_3 + 3\,TiO_2$ mechanically treated for 3 to 12 h do show broadened characteristic peaks of the $Bi_4Ti_3O_{12}$ phase with a crystallite size of about 7 nm.[240] Raman spectra showed twelve out of sixteen or twenty four possible ones (depending on the symmetry of the phase, tetragonal or orthorhombic) ascribed to the $Bi_4Ti_3O_{12}$ structure. Probably, here one deals with a disordered, loose, weakly layered structure, which undergoes ordering on calcination under mild conditions before the formation of the $Bi_4Ti_3O_{12}$ phase rather than the layered structure with the unit cell parameter $b = 32.815$ Å. The lone electron pair of Bi^{3+} ions is responsible for the variety of possible coordinations with variation of the Bi – O distances, which provides the possibility for partially ordered structures with large unit cell parameters to form in the course of mechanochemical synthesis. Probably, the authors of study [240] found an appropriate combination of the parameters of mechanical loading and the fineness of the starting reactants. In cannot be ruled out that unavoidable heating during mechanical treatment led to partial crystallisation of the product (the mill design and procedure for mechanochemical synthesis were not reported in detail).

Mechanochemical synthesis of nanocrystalline complex oxide $CaBi_4Ti_4O_{15}$ after mechanical treatment in nitrogen atmosphere for 30 h was reported.[241] However, other studies reported that mechanical treatment only led to preparation of precursors of layered compounds (Aurivillius phases), that is, solid solutions $(SrBi_2Nb_2O_9)_{1-x}(Bi_3TiNbO_9)_x$ with $x = 0.35$ and 0.65 [242] and Bi_3TiNbO_9 [90] upon soft calcination or hot pressing accompanied by the formation of ceramics with oriented grains. Similar results were also obtained for the $SrBi_2Ta_2O_9$ phase.[243] However, calcination of an amorphous precursor synthesised by mechanical treatment for 10 to 50 h did not lead to ordering (small-angle reflections were almost no indicated). Stabilisation of disordering in the layered perovskites has long been observed in HTSC-materials.[30, 226] This effect can play a negative role in ferroelectrics. A study [244] also reported mechanochemical synthesis of a layered compound

LiV_3O_8, but the X-ray diffraction patterns showed no (00*n*) peaks corresponding to the layered structure.

7. Scheelites

Almost all feasible binary oxides with the scheelite structure were prepared in two studies.[19,81] Experience has shown that the choice of the systems $MO + MoO_3$ (WO_3) as a model class for quantitative investigation of the dynamics of mechanochemical synthesis was right, because at smaller difference between the ionic radii of the reactants, the products of mechanochemical synthesis show disordering in the cationic sublattice. It seems that scheelite-type oxides of more complex chemical composition were not prepared by mechanochemical synthesis due to the lack of practical applications.

8. Other structural types

Studies of mixtures of lead oxides[245] gave Pb_2O_3 and minium in the form of solid solutions $Pb_3O_{4\pm x}$ in the reactions

$$PbO + PbO_2 \longrightarrow Pb_3O_4,$$

$$Pb_3O_4 + PbO_2 \longrightarrow Pb_2O_3.$$

Mechanochemical synthesis of monophase samples of these phases is hardly probable because of equilibrium between mass transfer in the secondary loading events and mechanolysis of oxides.

Cubic $BaCuO_2$ with the structure similar to the known one (PDF 38-1402) was prepared by mechanical treatment of $BaO_2 + CuO$ and $2\,BaO_2 + Cu_2O$ compositions in an AGO-2 mill for 30 min.[26]

Tojo *et al.*[247] studied mechanochemical synthesis using mixtures $Bi_2O_3 + A_2O_5$ (A = V, P, Sb)[246] and $Cr_2O_3 \cdot n\,H_2O + A_2O_5$ (A = V, Sb).[247] In all cases they prepared monophase products $BiVO_4$, $BiPO_4$, $BiSbO_4$, $CrVO_4$ and $CrSbO_4$ upon treatment for 2 to 6 h. The compounds $CrAO_4$ were assigned the rutile structural type. Rare-earth element oxide vanadates RVO_4 (R = Y, Nd, Sm, Gd, Dy and Er) assigned to the zircon and high pressure scheelite structural types were prepared under similar conditions.[248]

Mechanochemical synthesis in the Bi–V–O system following the reaction[82]

$$Bi_2O_3 + V_2O_5 \longrightarrow BiVO_4.$$

gave monophase samples with the structure of clinobisvanite $BiVO_4$ [primary product, $a = 5.166(4)$ Å, $b = 5.094(4)$ Å, $c = 11.675(8)$ Å, $\gamma = 90.25^\circ$ at $E_s = 78$ MJ kg^{-1}, space group $I2/b$ (15)]. Clinobisvanite is a product of the reaction

$$Bi_2O_3 + 2\,VO_2 \longrightarrow BiVO_4 \longrightarrow BiVO_4 + \gamma\text{-}Bi_2VO_5,$$

Prolonged treatment results in the formation of an Aurivillius phase. Unusual EPR spectrum of V^{4+} in monophase clinobisvanite powder is due to its structure and high concentration of vacancies.[82]

Eulytite $Bi_4Ge_3O_{12}$ [$a = 10.517(5)$ Å at $E_s = 40$ MJ kg^{-1}, space group $I\bar{4}3d$ (220)] is formed in a similar system $Bi_2O_3 - GeO_2$ as the secondary product of mechanochemical synthesis by the reaction[108]

$$2\,Bi_2O_3 + 3\,GeO_2 \longrightarrow Bi_2GeO_5 \longrightarrow Bi_4Ge_3O_{12}.$$

Compounds $CaSb_2O_4$ [$E_{1/2} = 3.8(6)$ MJ kg^{-1}, $a = 9.245(8)$ Å, $c = 9.483(8)$ Å, PDF 29-292] and $Ca_2Sb_2O_5$ (PDF 20-208) were identified as the primary and secondary phase, resepctively, in a study of mechanochemical reactions in the ternary system $CaO - Sb_2O_3 - Bi_2O_3$.[107]

An attempt to fabricate piezoelectric materials based on compounds of the $PbO - ZnO - Nb_2O_5$ system by mechanochemical synthesis led to columbite $ZnNb_2O_6$ [$E_{1/2} = 10(3)$ MJ kg^{-1}, PDF 76-1827] and changbaiite $PbNb_2O_6$ [secondary product, $E_{1/2} = 23(5)$ MJ kg^{-1}, PDF 29-780] following the reactions[135]

$$ZnO + Nb_2O_5 \longrightarrow ZnNb_2O_6,$$

$$PbO + Nb_2O_5 \longrightarrow Pb_2Nb_2O_7 \longrightarrow PbNb_2O_6.$$

Milling of a mixture $La_2O_3 + 2\,MoO_2$ in a planetary mill with WC/Co balls for 12 h led to a known compound $La_2Mo_2O_7$ (PDF 35-1476);[22] whereas mechanical treatment of a mixture $La_2O_3 + 2\,MoO_3$ gave a new phase of composition $La_2Mo_2O_{8.5-x}$ [$a = 10.5003(6)$ Å, $b = 16.982(1)$ Å, $c = 6.6218(4)$ Å; $\beta = 110.158(4)^\circ$, space group $C2/m$] (see Table 1).

Hexagonal phases β-Ln_2TiO_5 were prepared[197–199] by mechanical treatment of $Gd_2O_3 + TiO_2$ and $Dy_2O_3 + TiO_2$ mixtures with balls made of stabilised zirconium ceramics. The unit cell parameters of the phases are as follows: $a = 3.668$ and $c = 11.908$ Å (PDF 34-1307) for Gd_2TiO_5 and $a = 3.626$ and $c = 11.799$ Å (PDF 34-1445) for Dy_2TiO_5. This allows the corresponding structures to be treated as layered. Other structures known for these compositions include orthorhombic phases [PDF 21-342 and 34-1445, space group *Pnam* (62), $a = 10.49$ Å, $b = 11.26$ Å, $c = 3.70$ Å for Dy_2TiO_5] and cubic phases [space group $F\bar{4}3m$ (216), PDF 76-4, and $Fd3m$ (227), PDF 40-974]; they were not detected upon mechanical treatment, which is quite unusual. Disordering and coalescence usually favour the formation of phases of higher symmetry in the course of mechanochemical synthesis.

A hexagonal phase of composition $\sim Hg_2TlO_3$ with the unit cell parameters $a = 5.52$ and $c = 3.33$ Å was prepared after prolonged mechanical treatment of a mixture $4\,HgO + Tl_2O_3$,[26] *i.e.*, the formation of this phase is due to reduction.

Studies on the dynamics and products of mechanochemical transformations in the systems $PbO - MoO_3$ (Ref. 105) and $PbO - WO_3$ (Refs 19 and 20) led to the known phases Pb_2MoO_5 and Pb_2WO_5. A new phase characterised by large unit cell parameters and low symmetry was found in the system $ZnO - MoO_3$;[20] this can be related to reduction of oxides, first of all MoO_3.

The largest number of new phases prepared by mechanochemical synthesis was found in systems containing vanadium oxides. Mechanochemical reactions were comprehensively studied[20,249] in mixtures of the lead and vanadium oxides at different Pb : V ratios (Pb : V = 0.25–4) while products were characterised by powder X-ray diffraction and by NMR and EPR spectroscopies. The formation of at least five phases was disclosed, all of them being previously unknown. Two phases, the primary phase and the secondary one, were obtained as monophase powders following the reactions

$$PbO + V_2O_5 \longrightarrow Pb_4V_2O_{9-x},$$

$$Pb_4V_2O_{9-x} + VO_2 \longrightarrow Pb_7V_9O_{30-x}.$$

$Pb_4V_2O_{9-x}$ has a triclinic structure (space group $P1$), while $Pb_7V_9O_{30-x}$ has a monoclinic one ($P12/m1$). These compounds show almost all unusual structural features characteristic of the metastable phases prepared by mechanochemical synthesis. These phases are formed on different pathways of mechanochemical synthesis and include polyvalent cations (Pb^{2+}, Pb^{4+}, V^{5+}, V^{4+}, V^{3+}). Assuming, as usually, that the

amorphous and ordered states have the same compositions, the structural formula of the monoclinic phase is as follows: $Pb^{2+}_{3.25}Pb^{4+}_{0.25}V^{4+}_{0.5}(VO_4)^{3-}_{2.5}(V_2O_7)^{4-}_{0.75}$ (according to powder X-ray diffraction, EPR and NMR spectroscopy data).

A number of sodium and potassium vanadates were prepared by Molchanov *et al.*[250] New mechanochemically synthesised compounds whose peaks were not identified were found in the system $MoO_3-V_2O_5$.[25] Difficulties in determination of the structure of vanadates are due to a large number of possible structural elements based on vanadium. For instance, an EPR and NMR study of a mechanically activated, catalytically active system $V_2O_5-TiO_2$ revealed nearly ten different states of vanadium.[251]

A mixture of garnet $Y_3Al_5O_{12}$ and perovskite $YAlO_3$ was prepared by mechanochemical synthesis from a mixture of Y_2O_3 with the product of partial decomposition of $Al(OH)_3$ on heating to 673–873 K; the major component of the product was γ-Al_2O_3.[103] Mechanochemical interaction with corund (Mohs hardness 9) does not occur. Low-temperature decomposition of $Al(OH)_3$ leads to formation of metastable vacancy-rich structures with lower hardness and therefore mechanochemical transformations become possible.

Solid solutions of composition $Ba_2Na_{1+x}Li_xNb_5O_{15}$ with the tungsten bronze structure were first obtained upon prolonged (to 48 h) mechanical treatment of a mixture of oxides including BaO_2, Nb_2O_5, Na_2CO_3 and Li_2CO_3.[252] The mass loss during calcination was 9%, (thermogravimetric analysis data) and contamination of iron on milling was as high as 4.25%. Comparison of the quality of ceramics sintered from powders prepared by mechanochemical synthesis and conventional solid-phase reactions was not performed.

An attempt to prepare forsterite Mg_2SiO_4 by mechanochemical synthesis from a mixture of MgO and zeolite A was made;[253] however, it only gave an amorphous precursor from which the forsterite structure formed at $\sim$1250 K.

Apatite occupies an intermediate position between salts and oxides. However, since the discovery of high oxygen conductivity in rare-earth element oxide silicates with the apatite structure[254] it is more appropriate to consider this structural class along with oxides. An attempt[255] to prepare $La_2Si_2O_7$ by mechanical treatment of a mixture of oxides for 3 h only led to an amorphous precursor, whereas the apatite structure formed on heating. However, Fuentes reported mechanochemical synthesis of nanocrystalline apatite ($D \approx 10$ nm) of composition $La_2Si_2O_7$ by mechanical treatment of amorphous silica gel or cristobalite and La_2O_3 for 6–18 h.[74, 75, 256] The SiO_2 polymorphs showed very similar reactivities. In this case the comparison of forsterite and apatite again proves that the molecular masses of the reactants govern the dynamics of mechanochemical synthesis. For instance, the synthesis of lanthanum germanate $La_{10-x}(GeO_4)_6O_{3-1.5x}$ with the apatite structure for only 6 h by mechanical treatment of a mixture of oxides was reported.[257] A large number of solid solutions based on apatite-like phosphates of different composition were prepared by Chaikina.[258, 259] Interest in phosphates is increased in connection with the preparation of biocompatible materials. Mechanochemical synthesis is of interest as anhydrous method of preparation of hydroxyapatites.[260, 261] Phosphates have a broad spectrum of industrial applications as fluorescent materials, pigments, catalysts, materials for coatings, *etc*. Mechanochemical synthesis was used[262] for preparation of amorphous precursors of neodymium-doped diphosphate $Mn_2P_2O_7$ from the mixture $NH_4H_2PO_4 + MnCO_3 + Nd_2O_3$.

Mechanochemical interactions in the system $MgO + B_2O_3$ [$B(OH)_3$] were studied.[263] It was found that the reactions only occur in the presence of boric acid and that anhydrous magnesium borates are only formed from mechanically activated mixtures $MgO + B_2O_3$ under soft annealing.

Methods of preparation, characterisation and the applications of the ceramics–ceramics and ceramics–metal (cermets) composites are similar. Now we will analyse a number of studies in this field. ZnO-Varistors represent composites comprised of three phases including zinc oxide, spinel and the intergrain phase based on Bi_2O_3. It was found that mechanical treatment of the mixture of starting oxides leads to formation of not only nanosized composites, but to doping of ZnO.[264] The properties of the material were significantly improved. Similar results were also reported in a study[265] where zinc oxide was doped with Al_2O_3 and In_2O_3 by mechanical treatment of a mixture of ZnO, Al_2O_3 and In_2O_3. This resulted in a semiconductor that increases the efficiency of hybrid solar cells (devices for transformation of solar energy to electric energy).

Fourteen nanocomposites were prepared from high-mixed-conductivity complex oxides with the perovskite and fluorite structures and their compatibility on sintering was evaluated.[266] Sintering of composites until a dense state is only possible for powders with optimised granulometric composition and at optimal sintering temperature and duration. As the sintering duration exceeded 1 min, the density of ceramics decreased. Dense ceramics based on composites are of great interest to design of multilayer selective membranes in CMR while porous ceramics can be used as electrode materials. Mechanochemically synthesised metastable phases of supersaturated solid solutions or amorphous states, which can spontaneously form 'core–shell' nanocomposites on annealing or sintering, are quite promising for CMR.[181] Nanostructured cermets possess a combination of properties that are usually typical of either metals (high electrical and thermal conductivity, low friction coefficient, plasticity) or oxide ceramics (wear resistance, high-temperature stability, mechanical strength, *etc*.). Oleszak *et al.*[267, 268] prepared composites with the metallic matrix $Cu-Al/Al_2O_3$ form the systems $CuO-Al$ or $Cu_2(OH)_2CO_3-Al$ under different treatment conditions. The redox reactions occurring on mechanical treatment involve the formation of intermediate phases [intermetallics and solid solution Cu(Al)]. A number of composites including $Cu-Al_2O_3$ and $NiAl-Al_2O_3$ were prepared and characterised by Murty.[269] The composites $Fe_2O_3-Al-Fe$ and $Fe_2O_3-Al-Mg_2Si$ were studied[270–272] as promising structural materials. Travitzky *et al.*[273] reported mechanochemical synthesis of reinforced Ni-based corundum composites. Cermets are of interest as porous catalyst supports.[274, 275] A complex alloy $Ti-Ru-Fe-O$ prepared[276] by mechanochemical synthesis shows good electrochemical characteristics and thus seems to be promising as electrode material. Nanocomposites Sn and Sb in SiO_2 matrix were prepared by mechanical treatment of mixtures $SnO + Si$ and $Sb_2O_3 + Si$ for 3–4 h.[277]

Most compounds prepared by mechanochemical synthesis ($\sim$98%) using complex oxides have structural analogues among minerals (see above). This again substantiates the correctness of theory of ultrafast mechanochemical synthesis of complex oxides, namely,[18, 29] crystalline products of mechanochemical synthesis are formed under highly nonequilibrium conditions, the deviations of the composition from ideal structural formula being very large. Eventually, diffraction techniques detect only those structural types which are highly tolerant to variations of the chemical composition, *i.e*., they

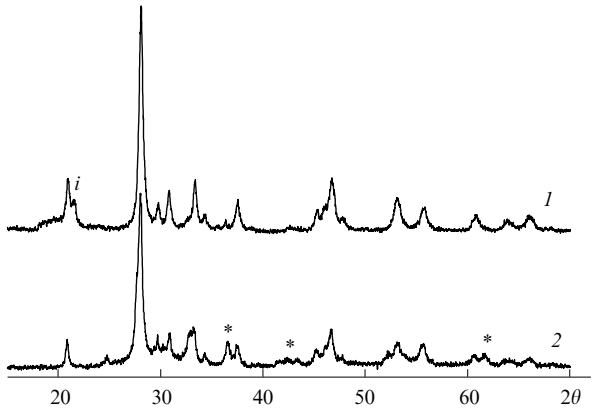


Figure 16. X-Ray diffraction patterns of mechanically treated $CuO + Bi_2O_3$ (*1*) and $Cu_2O + 2\,Bi_2O_3$ (*2*) samples (E_s = 30 MJ kg^{-1}, treatment duration 10 min).
Reflections of residual Cu_2O are asterisked; *i* denotes the sillenite reflection.

can readily form solid solutions (including those with different oxidation states of metals). Minerals are also formed in the nature under nonequilibrium conditions in complex chemical compositions. Therefore, the fact that the structural types of the compounds prepared by mechanochemical synthesis often match those of minerals should not be surprising. Moreover, this allows an inverse problem to be posed, namely, to prepare known minerals by mechanochemical synthesis.

To check this assumption, mixtures of oxides $CuO + Bi_2O_3$ and $Cu_2O + 2\,Bi_2O_3$ were subject to mechanical treatment to prepare $CuBi_2O_{4-x}$ with the structure of kusachiite [PDF 48-1886, space group $P4/ncc$ (130), a = 8.511, c = 5.823 Å]. Figure 16 presents the X-ray diffraction patterns of the products of mechanochemical synthesis. Indeed, they are almost monophase and have the kusachiite structure irrespective of the oxidation state of the copper atom in the oxide. The unit cell parameters are different [a = 8.509(3), c = 5.822(2) Å for $CuBi_2O_4$ and a = 8.524(3), c = 5.805(2) Å for $CuBi_2O_{3.5}$], which indicates a different content of oxygen in the crystal lattice and different size of copper ions. Thus, the kusachiite structural type is highly tolerant. This gives grounds to assume that mechanochemical synthesis can be used for preparation of other complex oxides belonging to this structural type.

VI. Conclusion

Born as an avenue of basic research, mechanochemistry of oxides undergoes a rapid transformation to a technique for fabrication of novel functional ceramic nanomaterials and catalysts with preset properties, electrode materials, fillers and composites. It is of particular importance that materials prepared by mechanochemical synthesis possess unique features that cannot be reproduced by other methods. As applied to materials prepared by mechanochemical synthesis, the term 'unique' is quite correct. The list of the structural types prepared by mechanochemical synthesis (note that the structural type is the key property-determining factor) includes three or four dozens of names, but is far from being exhausted. The analogy between products of mechanochemical synthesis and minerals will rapidly put new structural types and compounds on this list. The available semiquantitative theory of the threshold phenomenon (ultrafast mechanochemical synthesis of complex oxides) helps to make a correct choice of promising systems and to identify complex mechanochemical transformations despite a limited number and broadening of X-ray reflections. Based on this theory, one can not only perform target synthesis of materials, but also design highly efficient devices for preparation of nanopowders and synthesis of particular materials under mechanical loading above threshold.

Metastable character of mechanochemically synthesised compounds, which is well defined for binary oxides, often becomes increasingly less pronounced as the number of components increases; this makes it possible to prepare even metastable dense ceramics. This avenue of research, *i.e.*, the design of (i) metastable materials having known chemical compositions but new (different) structures or (ii) materials having new chemical compositions and known structures goes beyond the scope of traditional materials science. Nanocomposites fabricated from vacancy-rich metastable phases prepared by mechanochemical synthesis favour the search for novel methods of the design of nanomaterials (*e.g.*, a proton conductor from a mixture of $Ca_2Sb_2O_5$ and CaO [190]). Additional potential of mechanochemical synthesis can be practically implemented in the design of a specific kind of nanocomposites that form spontaneously due to decomposition of metastable states on annealing or sintering.[107, 181] Certain specific features of nanopowders prepared by mechanochemical synthesis (*e.g.*, inhomogeneity or strong aggregation) are usually treated as drawbacks of these system. However, they can appear to be very useful in some cases including the preparation of nanostructured ceramics, design of multilayer ceramic membranes, *etc*. High density of aggregates present in powders prepared by mechanochemical synthesis provide the best compaction and low shrinkage on sintering to the dense state, which is critical to the design of multilayer membranes, films, coatings and to some other applications. The mechanochemical ceramic method, which involves mechanochemical synthesis for preparation of desired compounds, is only one of a variety of modern methods suitable for fabrication of nanomaterials. However, only this method meets all modern requirements, namely, it provides the possibility of design of dry green technologies characterised by a relatively low cost of products and minimum energy expenditure.

The review has been written with the financial support from the Russian Foundation for Basic Research (Project Nos 95-03-08068, 99-03-32733, 02-03-33330 and 06-03-32131), the Siberian Branch of the Russian Acadeny of Sciences, the Interdisciplinary Integration Project of the Siberian Branch of the Russian Acadeny of Sciences and National Academy of Sciences of Ukraine (Project No. 95).

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