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Lanthanide Titanates

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Compounds formed in the R_2O_3-TiO_2 binary systems, where R is a lanthanide element, are examined. Methods for the preparation of lanthanide titanates in both polycrystalline and single-crystal form are analysed. Attention is concentrated on the crystal chemistry and the physicochemical properties of lanthanide titanates with quadrivalent titanium. A number of examples of practical applications of these compounds are given.
The bibliography includes 110 references.

CONTENTS

I.	Introduction	228
II.	The synthesis of lanthanide titanates	228
III.	High-temperature interaction of titanium dioxide with lanthanide sesquioxides	230
IV.	Crystal chemistry of lanthanide titanates	232
V.	Properties of lanthanide titanates	235
VI.	Examples of practical applications	240

I. INTRODUCTION

Interest in lanthanide titanates with the pyrochlore structure arose in connection with the suggestion that they might have ferroelectric properties—by analogy with cadmium pyroniobate $Cd_2Nb_2O_7$, which has a cubic structure of the pyrochlore type and is a unique and unusual ferroelectric material at low temperatures[1,2]. This finding stimulated the study by Roth[3], who was the first to synthesise and investigate a whole series of lanthanide titanates with the pyrochlore structure. Further investigations showed that only some titanates ($La_2Ti_2O_7$ and $Nd_2Ti_2O_7$)[4,5] are effective ferroelectric substances with extremely high Curie temperatures. However, numerous studies on the synthesis and properties of these compounds raised a series of new problems. Thus an investigation of the phase transformations in the high temperature interaction of TiO_2 with lanthanide sesquioxides established the formation of lanthanide titanates with different structures from which new technological materials with a set of interesting properties can be obtained. Their high fire resistance and chemical stability permits their employment in high-temperature chemistry and nuclear power engineering.

However, the available data have not been surveyed hitherto; a monograph[6] deals with only a small range of problems. The present review gives a systematic account of data concerning the methods of synthesis, crystal chemistry, and physicochemical properties of lanthanide titanates with quadrivalent titanium; only compounds formed in the R_2O_3-TiO_2 binary systems are considered.

II. THE SYNTHESIS OF LANTHANIDE TITANATES

A series of methods for the synthesis of lanthanide titanates in the polycrystalline and single-crystal form have now been developed.

1. Solid-Phase Synthesis

The solid-phase synthesis is carried out by heating to high temperatures mechanical mixtures of TiO_2 and lanthanide sesquioxides. In most cases discs are pressed from the mechanical mixtures and are then placed on platinum supports and annealed in electric furnaces in air.

Ceramic technology requires the use of high temperatures, prolonged annealing, and in addition repeated sintering of the product in order to obtain a single-phase titanate. Nevertheless this method of synthesis is widely used[3,7-16], but only as a rule in those cases where the aim was to obtain a compound of the type $R_2Ti_2O_7$ from a mechanical mixture of the oxides having the composition $2TiO_2 + R_2O_3$. This is apparently due to the advantageous feature of the method: the fact that one obtains a product with a more precisely specified composition and also because of the fairly high rate of formation of the given compounds. For example, the compounds $La_2Ti_2O_7$, $Nd_2Ti_2O_7$, $Sm_2Ti_2O_7$, $Gd_2Ti_2O_7$, $Dy_2Ti_2O_7$, and $Y_2Ti_2O_7$ have been obtained[3] by heat treatment for 4 h at 1100°C. However, the same compounds have been synthesised at different temperatures in a number of studies. For example, $Sm_2Ti_2O_7$ has been obtained at 1200°, 1300°, and 1400°C[3,7] and $Gd_2Si_2O_7$ at 1000°, 1350° and 1400°C[3,7], the duration of sintering being determined by the temperature of the synthesis.

2. The Coprecipitation Method

Numerous investigations[7,15,17-33] in the last decade showed that it is useful to obtain polycrystalline lanthanide titanates by coprecipitation and not for mechanical mixtures of oxides. Amorphous hydroxides are as a rule coprecipitated by treating a mixture of an aqueous solution of $TiCl_4$ and a nitric acid (or hydrochloric acid) solution of R_2O_3 with aqueous ammonia. The product is filtered off, washed with water, and dried at approximately 100°C. According to X-ray and electron diffraction data, the freshly obtained precipitates are amorphous. Their characteristic feature is the presence of a considerable amount of chemically bound lanthanide hydroxide. In the general case the rate of chemical reaction between the lanthanide and titanium at the instant of precipitation depends on the nature and composition of the precipitate formed; the amount of product which has reacted may range from 15 to 45%.[31]

Crystalline titanates are formed on further heating of mixtures of the amorphous hydroxides to the crystallisation temperature. Fig. 1*c* presents a thermogram of the coprecipitated neodymium and titanium hydroxides[22]. It is seen that two peaks are characteristic of the precipitated product: an endothermic peak at 290°C corresponding to

dehydration and an exothermic peak at 810°C corresponding to the crystallisation of $Nd_2Ti_2O_7$. It has also been established [22] that the thermograms of precipitates obtained by coprecipitation differ significantly from those of the individual lanthanum and titanium hydroxides, which enabled the authors [22] to suggest that coprecipitation results in the formation of the corresponding lanthanide titanate and not simply a mechanical mixture.

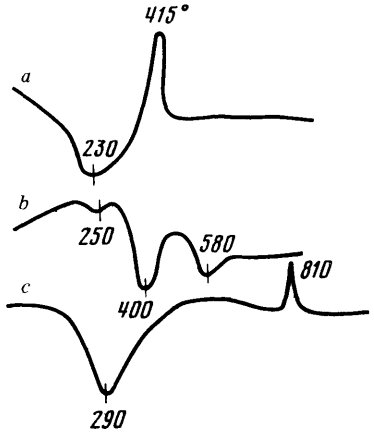


Figure 1. Thermograms: a) titanium hydroxide; b) neodymium hydroxide; c) coprecipitated neodymium and titanium hydroxides [22] (the numerals represent the temperature in °C).

A detailed study has been made [31] of the dehydration process, which showed that the products of the chemical reaction between titanium and lanthanide hydroxides are hydroxo-complexes $R_2[TiO_2(OH)_2]_3.nH_2O$. OH groups are eliminated at approximately 500°C and the residual water (1.5–2%) is lost at approximately the same temperature. The main bulk of water is eliminated at temperatures up to 150°C where the rate of dehydration is extremely high. Because of this, the authors [31] concluded that the interaction between the coprecipitated lanthanum and titanium hydroxides most probably involves the OH groups and proceeds via the hydroxo-complex stage.

The phases in the temperature range 400–800°C, i.e. from the temperature corresponding to the virtually complete removal of water up to the formation of lanthanide dititanates, have been identified [30,31]. The existence of intermediate compounds having the composition $La_{2/3}TiO_3$ having the perovskite structure and crystallising in the orthorhombic system has been established. According to the authors [31], lanthanide metatitanates are the intermediate products which are formed on heating the coprecipitated hydroxo-complexes of the lanthanide and titanium. These compounds are unstable and decompose above 800°C with formation of lanthanide dititanates. It is noteworthy that analogous defect phases having the perovskite structure have been detected earlier on interaction of La_2O_3 and TiO_2 in a reducing atmosphere [33–35]. However, the unit cell parameters of perovskite were in this case [31] somewhat smaller than in the study of Leonov et al. [35] This was explained [31] by the failure to complete the formation of the lattice in the compounds $R_{2/3}TiO_3$ obtained by the moderate heating of the coprecipitated hydroxides.

The temperature of the synthesis of lanthanide titanates is usually somewhat higher than their crystallisation temperature. Thus $Nd_2Ti_2O_7$ and $La_2Ti_2O_7$ crystallise at 810° and 825°C, while the compounds have been synthesised by different workers in the temperature range 1000–1300°C. This is also true of the titanates of the entire lanthanide series. The degree of formation of $La_2Ti_2O_7$ has been studied [21] as a function of temperature and duration of annealing. It was established that the temperature rather than the duration of annealing has a considerable influence on the yield of $La_2Ti_2O_7$. The intensity and distinctness of the lines on the X-ray diffraction patterns increase with temperature for different durations of heat treatment in the range from 1 to 12 h, but above 1100°C they hardly change. At 900°C the complete formation of $La_2Ti_2O_7$ requires an annealing time of 6 h.

Thus the clear advantages of the coprecipitation method are a reduction of the temperature of the synthesis of the compounds and the possibility of the virtually complete binding of R_2O_3 and TiO_2, which can probably be explained by the formation of lanthanide titanates already in the coprecipitation process [22,27].

Phase transformations in the ageing of a charge comprising the coprecipitated hydroxides in air under normal conditions have also been investigated [31]. The investigation showed that the nature of the processes occurring on heating a charge of coprecipitated lanthanide and titanium hydroxides differs from that of the processes occurring during their storage, although the overall composition of the products may be the same in both cases. Thus, when the charge is heated, the chemical interaction between the components proceeds via the hydroxo-complex stage with formation of lanthanide titanates. In the second case (during the ageing of the charge) the hydroxo-complexes of the lanthanide and titanium decompose with the ultimate formation of the individual oxides R_2O_3 and TiO_2.

3. The Method Based on the Decomposition of Nitrate Salts

The technology of the synthesis of lanthanide titanates (for lanthanides ranging from La to Lu and Y) by the thermal decomposition of the nitrate salts has been described [36,37]. The starting materials were the lanthanide oxides and the salt $TiO_2(NO_3)_2.6H_2O$, which were dissolved in separate vessels in hot dilute HNO_3 solutions, which were filtered and then mixed. The resulting solutions were evaporated until the crystallisation of the salt and then heated at 500°C (5–10 h) in order to remove nitrogen. The completion of the reaction was tested by X-ray diffraction and chemical analyses.

It was established [36,37] that lanthanide titanates (2–10% yield) are formed at the instant of the decomposition of the nitrate salts. During annealing, the yield is 55–77% at 900°C and 81–90% at 1200°C. The completion of the reaction requires additional heat treatment at 1500–1600°C for 3 h; after this, the substances did not contain the free oxides. Like the coprecipitation method, the above procedure made it possible to carry out the initial stage of the synthesis at lower temperatures, but in addition it eliminates the operation of filtration and washing of the precipitates.

4. Synthesis of Lanthanide Single Crystals

In the synthesis of lanthanide single crystals the main problem is the attainment of the melting point (approximately 2000°C), which requires a complex apparatus; the problems of the selection of crucibles and the atmosphere for the synthesis are no less important.

According to the literature[38-51], lanthanide titanate single crystals are synthesised by a wide variety of methods, both high-temperature (the Verneuil method, zone fusion, etc.) and low-temperature (hydrothermal, in solution, and in the melt) methods.

(a) High-temperature methods. The Verneuil method, which consists in passing a fine powder of the initial substance through the flame of an oxygen–hydrogen burner, can apparently be regarded as the main high-temperature method for the growing of lanthanide titanate single crystals. After fusion in the flame, droplets of the substance fall on to the upper part of the growing crystal. Crystallisation can begin either on portions of the prefused and crystallised substance or (preferably) on a seed crystal introduced beforehand[52]. La_2TiO_5 [38] and $Nd_2Ti_2O_7$ [46] have been obtained in this way.

In the course of its application to the synthesis of single crystals from refractory oxides the Verneuil method has undergone a series of changes. The improvements involve mainly the heating apparatus. A plasma or electric arc furnace has replaced the oxygen burner. Nd_2TiO_5 [39] and $La_2Ti_2O_7$ [44] single crystals have been grown by the Verneuil method in combination with a plasma furnace.

A vertical version of the zone fusion method (or the floating zone method), which eliminates the possibility of the contamination of the product by the substance of the boat, has been used[4,53] to grow $La_2Ti_2O_7$ and $Nd_2Ti_2O_7$ single crystals. Heating was achieved with the aid of a reflection furnace. The crystal is grown by moving the fused zone down a rod of the initial substance clamped at both ends. The quality of the crystal is determined mainly by the rate of migration of the zone. $La_2Ti_2O_7$ and $Nd_2Ti_2O_7$ single crystals were grown at zone velocities of 10 and 5 mm h^{-1} respectively.

Among the high-temperature methods for the growing of lanthanide titanate single crystals, the method of direct high-frequency fusion in a cold container, developed at the Lebedev Physical Institute of the USSR Academy of Sciences[54], merits attention. The technological process includes three stages: (1) the preparation of the "seed" melt, which can be achieved by means of an additional source of heat; (2) gradual fusion under the influence of a high-frequency field of the entire charge with the exception of a thin layer directly adjoining the water-cooled walls of the container; (3) slow directional crystallisation of the melt by a gradual decrease of the power of the high-frequency generator or by lowering the container relative to the inductor[54]. The fundamental advantage of the new technology is the absence of contact between the melt and chemically different materials, which ensures a high chemical purity of the product.

Single crystals of almost all the lanthanide titanates, having the general formula $R_2Ti_2O_7$ (except for R = Ce or Pm), have been synthesised in this way[55]. The size of the crystals was 2–12 mm, which enabled the authors to investigate a whole series of their physicochemical properties.

(b) Low-temperature methods. Preference has been given recently to low-temperature methods in which crystals are grown during deposition from solution. Depending on the nature of the solvent, different versions of the method are possible. In a non-aqueous solvent crystals are grown from solution in the melt; if the solvent is water, then the hydrothermal method, based on a high-pressure technique, is suitable for refractory oxides insoluble in water at atmospheric pressure[52]. The following titanates have been obtained by growing from solution in the melt; $R_2Ti_2O_7$ (R = Sm, Eu, Gd, Tb, Ho, Er, or Y)[40,47,48,49]; R_2TiO_5 (R = Dy or Gd);[40] $Nd_2Ti_2O_7$ and $La_2Ti_2O_7$.[50]

Titanates of the type $R_2Ti_2O_7$ have been synthesised[40] in platinum crucibles with closely fitting lids at a constant temperature of 1235°C in the course of 1 week (in order to concentrate the solution by evaporating the solvent); lead oxide PbO was used as a flux. The isotropic crystals obtained had a well-defined octahedral shape (with a diameter of 3 mm). Another variety of the method was used in the same study[40] to synthesise single crystals of the type R_2TiO_5: an increase of the concentration of the solution was achieved by its slow cooling from 1280° to 940°C at a rate of 3 K h^{-1}. Analysis showed that the crystals obtained (lamellar or rod like, up to 3 mm in length) contained 4% of PbO as an impurity. The same variety of the method—slow cooling until the formation of a saturated solution—was used in other studies[47,49,50]. However, careful study of the crystals obtained by Weissenberg's method[50] revealed the occurrence of twinning in the crystals, which significantly hindered their further structural investigation.

The hydrothermal method for the growing of lanthanide titanate crystals has been used in only two studies[32,42] for the synthesis of single crystals of the type R_2TiO_5 (R = Nd, Sm, Dy, or Yb). Mechanical mixtures with the ratio $TiO_2:R_2O_3 = 1:1$, placed in silver tubes, were put in exoclaves of the type designed by Sternberg. The synthesis was carried out over a period of 50–100 h at 700°C and 1000–2000 atm. The solvent was an aqueous 8% NH_4F solution. The crystals obtained were prismatic and their size ranged from 0.1 to 0.5 mm. Shcherbakova et al.[42] also quote the calculated lattice parameters of Nd_2TiO_5, which agree well with other published values for this compound[39]. The small size of the crystals of other titanates R_2TiO_5 precluded structural investigation.

In conclusion one should note yet another method, used[41] to prepare Y_2TiO_5 single crystals. The method is based on the solid-phase reaction between Y_2O_3, TiO_2, and sodium oxalate, which occurs at 1300°C in a sealed tube; the $NaYTiO_4$ formed, having a structure of the K_2NiF_4 type, decomposes on further heating in air at 1500°C and is a heterogeneous product containing a certain number of very small transparent acicular Y_2TiO_5 crystals.

III. HIGH-TEMPERATURE INTERACTION OF TITANIUM DIOXIDE WITH LANTHANIDE SESQUIOXIDES

The interaction of TiO_2 with lanthanide sesquioxides in systems where R = La, Gd, Dy, Er, Yb, or Y has now been investigated in greatest detail; phase diagrams have been constructed for these systems[11,14,15,19,57-59]. The interaction of TiO_2 with other lanthanide oxides has been scarcely investigated; data are available only concerning the isolation in a pure state of certain individual phases.

It is noteworthy that the phase diagrams of the TiO_2–R_2O_3 systems are fairly complex and, despite common features, differ significantly for different lanthanides. As an illustration, one may consider the phase diagrams of the TiO_2–Gd_2O_3, TiO_2–Y_2O_3, TiO_2–Er_2O_3, and TiO_2–Yb_2O_3 systems (Figs. 2–5). Evidently the compounds $R_2Ti_2O_7$, typical for all the remaining lanthanides, exist in the range of compositions close to 33 mole % R_2O_3. However, their crystal structures are not the same; in the range from samarium to lutetium and yttrium the $R_2Ti_2O_7$ structure is cubic and of the pyrochlore type (space group $Fd\,3m$); $La_2Ti_2O_7$, $Nd_2Ti_2O_7$, and $Pr_2Ti_2O_7$ crystallise in the monoclinic system (space group $P2_1$). According to a number of data[57,58,60,61], $Gd_2Ti_2O_7$, $Y_2Ti_2O_7$, $Er_2Ti_2O_7$, and $Tb_2Ti_2O_7$ melt congruently, at 1820° C, > 1900°, 1980°, and 1860° C respectively.

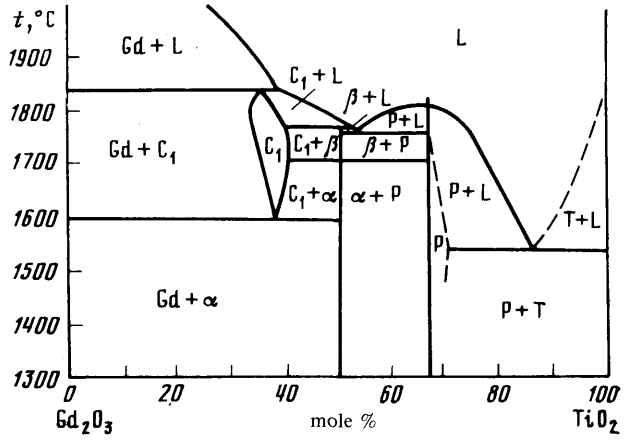


Figure 2. Phase diagram for the Gd_2O_3–TiO_2 system[14]; notation: Gd = Gd_2O_3 (solid solution); T = TiO_2 (solid solution); P = $Gd_2Ti_2O_7$ (pyrochlore); α and β = low- and high-temperature forms of Gd_2TiO_5; C_1 = face-centred cubic solid solution; L = liquid.

The differences between the ionic radii of the elements in the lanthanide series do not apparently influence the region of homogeneity for different $R_2Ti_2O_7$. The smaller scope for the substitution by titanium of "large" lanthanide ions in the range from lanthanum to gadolinium, associated with this fact, leads either to the formation of narrower regions of homogeneity (for example, approximately 3–5 mole % for $Gd_2Ti_2O_7$) or to their complete absence ($La_2Ti_2O_7$). With decrease of ionic radius, the width of the regions of homogeneity of the compounds $R_2Ti_2O_7$ grows, reaching 12 mole % for $Yb_2Tb_2O_7$. The considerable expansion of the region of homogeneity of the phases with the pyrochlore structure in the Dy_2O_3–TiO_2 and Y_2O_3–TiO_2 systems[19,57] at temperatures $\gtrsim$ 1700° C apparently indicates the influence in this case of factors other than the size factor. Figs. 2 and 3 show that the composition with 50 mole % R_2O_3 in the given systems corresponds to the compounds Gd_2TiO_5 and Y_2TiO_5. Compounds of a similar type (R_2TiO_5) are also characteristic of the entire series of lanthanides and as a rule exist in two polymorphic forms: the low-temperature orthorhombic α-form and the high-temperature hexagonal β-form. Only the high-temperature modification of Er_2TiO_5 has a cubic structure of the fluorite type[58]. However, according to the data of Leban et al.,[56] the compound Er_2TiO_5 was not detected in the study of the phase transformation in the Er_2O_3–TiO_2 system in the temperature range 1500–1600° C. Instead two cubic solid solutions of the pyrochlore and fluorite type, undergoing an interconversion at 50 mole % Er_2O_3, were found. The similarity of the structural types of the cubic phases formed at high temperatures in this system was apparently reflected in the interpretation of the data[56,58] and requires further elucidation and investigation of the system.

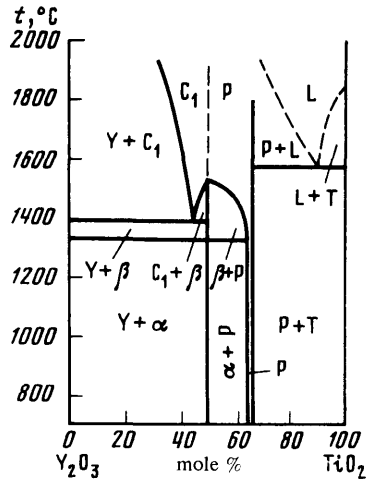


Figure 3. Phase diagram for the Y_2O_3–TiO_2 system[57]; notation: Y = Y_2O_3 (solid solution); T = TiO_2 (solid solution); P = $Y_2Ti_2O_7$ (pyrochlore); α and β = low- and high-temperature forms of Y_2TiO_5; C_1 = cubic solid solution with the fluorite structure; L = liquid.

It is of interest to note a difference in the behaviour of R_2TiO_5 at high temperatures as a function of the nature of the lanthanide[11,14,19,57,58,59]. Thus La_2TiO_5 is a stoichiometric compound, which melts congruently; Gd_2TiO_5 melts incongruently; Dy_2TiO_5 and Y_2TiO_5 are converted at high temperatures into a solid solution of the pyrochlore or fluorite type respectively and the phase diagram of the Yb_2O_3–TiO_2 system altogether fails to reveal the existence of the compound Yb_2TiO_5, as can be seen from Fig. 5. The compounds $2La_2O_3.9TiO_2$ and Yb_6TiO_{11}, which do not arise in other systems, also exist in the La_2O_3–TiO_2 and Yb_2O_3–TiO_2 systems (with the maximum and minimum ionic radii of the lanthanide).

All the diagrams presented in the regions of compositions where the R_2O_3 content reaches up to 33 mole % correspond to simple eutectic systems (the eutectic temperatures and compositions are listed in Table 1). When the R_2O_3 content exceeds 50 mole %, there is a broad region of a cubic solid solution of the fluorite type (C_1), the lattice parameters of these solutions being a function of composition. The existence of a narrow single-phase

region (~ 1 mole %) of a cubic solid solution having a structure of the type Tl_2O_3 (C_2) has been noted only for R = Dy, Er, or Yb.

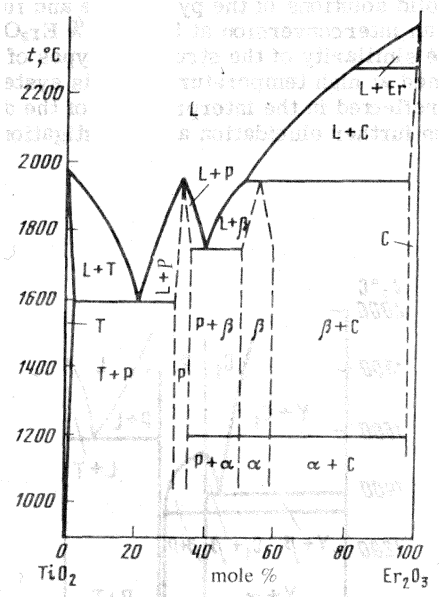


Figure 4. Phase diagram for the Er_2O_3–TiO_2 system [58]; notation: Er = Er_2O_3 (solid solution); T = TiO_2 (solid solution); P = $Er_2Ti_2O_7$ (pyrochlore); α and β = low- and high-temperature forms of Er_2TiO_5; C = solid solution of Mn_2O_3 type; L = liquid.

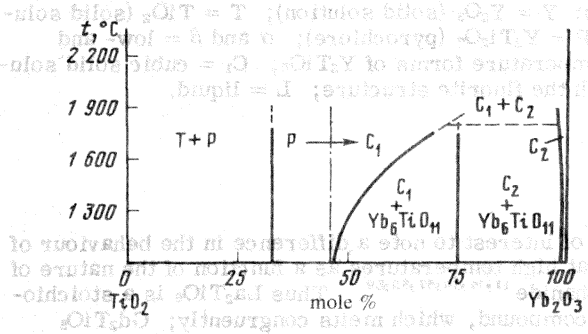


Figure 5. Phase diagram for the Yb_2O_3–TiO_2 system [59]; notation: P = $Yb_2Ti_2O_7$ (pyrochlore); T = TiO_2 (solid solution); C_1 = cubic solid solution with the fluorite structure; C_2 = cubic solid solution of the Tl_2O_3 type.

The presence of such narrow regions of solid solutions was established in the Er_2O_3–TiO_2 system [58] only in connection with the study of a diffusion-dependent interaction involving single-crystal specimens. The diffusion research technique, first used for the TiO_2–Er_2O_3 and TiO_2–Y_2O_3 systems [58,62], undoubtedly made it possible to obtain more complete information about the characteristics of the high-temperature interaction in oxide systems.

IV. CRYSTAL CHEMISTRY OF LANTHANIDE TITANATES

In the first studies [3,13] which initiated the systematic investigation of systems based on TiO_2 and R_2O_3 it was already established that many mixtures of these oxides, taken in proportions of 2 : 1, give rise to the compounds $R_2Ti_2O_7$ with a pyrochlore type structure after appropriate heat treatment. It was found in later investigations [3,19,33,63] that such compounds do indeed exist for lanthanides whose ionic radius satisfies the condition $1.22 < (r_{R^{3+}}/r_{Ti^{4+}}) < 1.5$.

Table 1. The eutectic temperatures and compositions in the R_2O_3–TiO_2 systems.

Composition	Eutectic compn. mole % R_2O_3	Eutectic temp., °C	Refs.
Gd_2O_3—TiO_2	13	1540	14
Tb_2O_3—TiO_2	14	1640	61
Er_2O_3—TiO_2	22	1550	58
Y_2O_3—TiO_2	10	1580	57

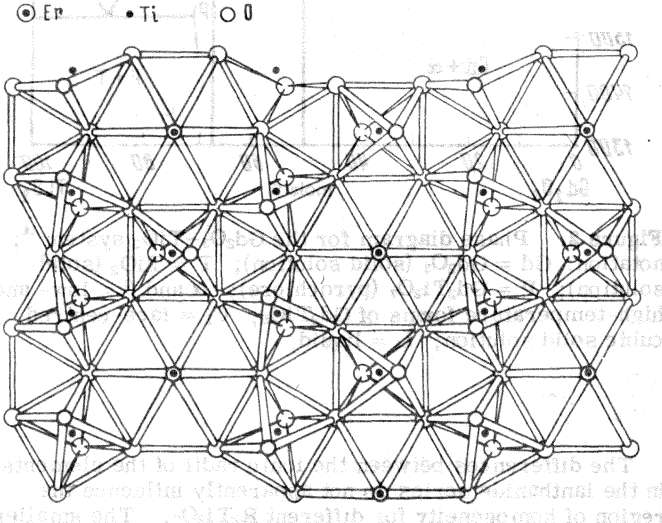


Figure 6. Projection of the pyrochlore structure ($Er_2Ti_2O_7$) [66] along a threefold symmetry axis.

This geometrical criterion, based on analysis of the ionic radius ratios from the standpoint of the theory of close packing, is defective according to some workers [64], because the interatomic interaction in pyrochlores is not purely ionic. However, for lanthanide titanates this criterion gives rise to no doubts. Thus in the $Nd_2O_3 + 2TiO_2$ composition, for which $r_{R^{3+}}/r_{Ti^{4+}} = 1.52$, there is no pyrochlore phase and the compound $Nd_2Ti_2O_7$ crystallises in the monoclinic system. This is also true of $La_2Ti_2O_7$. The remaining lanthanides (from samarium to lutetium) give rise to cubic $R_2Ti_2O_7$ structures of the pyrochlore

type[7-10,16,18,19,36,47,65-68]. There is also a linear correlation between the unit cell parameter a and the ionic radius $r_{R^{3+}}$.

The compounds $R_2Ti_2O_7$ (R represents elements from samarium to lutetium and yttrium) have the same structures as the mineral pyrochlore $NaCaNbTaO_6F$ with the structural formula $A_2B_2O_7$, where A represents sodium and calcium ions and B represents niobium and tantalum ions. Pyrochlore has a face-centred cubic lattice (space group $Fd3m$). The pyrochlore structure is derived[69] from the fluorite structure. When the fluorite structure is converted into the pyrochlore structure, one of each eight oxygen ions is removed from the anionic lattice sites, while the remaining ions are somewhat displaced from their ideal positions. The large A ions are coordinated to eight oxygen ions, which surround them, being located at the vertices of a distorted cube. The pyrochlore structure consists of a three-dimensional skeleton of distorted BO_6 octahedra joined together by their vertices. Series of mutually parallel chains joined by their vertices alternate with series of mutually parallel chains perpendicular to the chains of the first series. The octahedra of neighbouring chains are also joined together via their vertices (Fig. 6). The A ions and one seventh of the oxygen ions, which have not been displaced to the skeleton from the octahedra, are accommodated in the gaps between the octahedra.

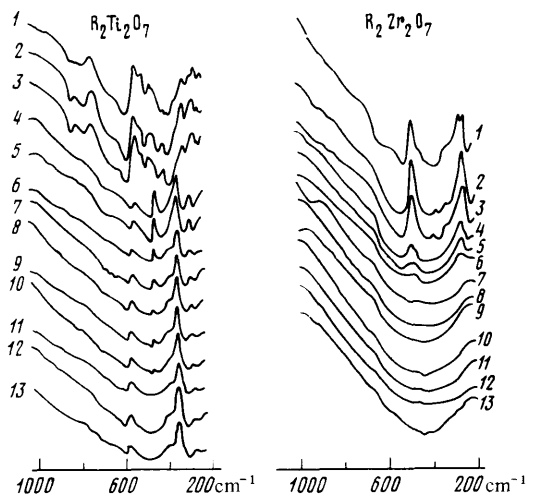


Figure 7. Infrared spectra of lanthanide titanates ($R_2Ti_2O_7$) and zirconates ($R_2Zr_2O_7$)[63]; R: 1) La; 2) Pr; 3) Nd; 4) Sm; 5) Eu; 6) Gd; 7) Tb; 8) Dy; 9) Ho; 10) Er; 11) Tm; 12) Yb; 13) Lu.

The transition from the fluorite structure to the pyrochlore structure is accompanied by the appearance on the X-ray diffraction patterns of superstructure lines corresponding to the establishment of order in the arrangement of the cations and the distortion of the oxygen polyhedra[65,67,69]. The ordering of pyrochlore phases is also indicated by the absorption maxima in the infrared spectra. Fig. 7 presents for comparison the infrared spectra of $R_2Ti_2O_7$ and $R_2Zr_2O_7$. In ZrO_2–R_2O_3 systems only certain compounds have the pyrochlore structure (R = Gd, Eu, Sm, Nd, Pr, or La). For lanthanide ions whose radii are smaller than the ionic radius of gadolinium, an ordered phase is not formed and Fig. 7 shows that in this case the infrared spectra are of a completely different type[63].

A characteristic feature of the phases of the pyrochlore type is their non-stoichiometry, which arises, on the one hand, when some of the Ti^{4+} ions are substituted by R^{3+} ions (this entails the formation of additional vacancies in the anionic sublattice), and, on the other, when some of the R^{3+} ions are replaced by Ti^{4+} ions. The general formula of the pyrochlore phases can be written as follows: $R_{2\pm x}Ti_{2\mp x}O_{7\mp x/2}\square_{1\pm x/2}$.[19]

In the series of lanthanide titanates, the $Er_2Ti_2O_7$ and $Y_2Ti_2O_7$ structures have been investigated most thoroughly[49,66] by X-ray and neutron diffraction methods (Fig. 6). The $Er_2Ti_2O_7$ unit cell contains 16 erbium ions at sites of trigonal symmetry. Each erbium ion is surrounded by 8 oxygen atoms, two of which lie diametrically opposite and are at a distance of 2.185 Å from the erbium ion, while the other six are arranged in the vicinity of the equatorial plane at a distance of 2.471 Å. The erbium ion in localised at the [common?] vertex of two diametrically opposite tetrahedra comprising erbium ions and in this respect the ions are equivalent, i.e. each erbium ion has six nearest neighbours at a distance of 3.562 Å. The Er–O–Er angle is 109°.

As mentioned above, compounds of the type $R_2Ti_2O_7$ are known also for the first members of the lanthanide series from lanthanum to neodymium (for which $r_{R^{3+}}/r_{Ti^{4+}} < 1.2$). However, in contrast to the compounds described above, which have a cubic structure of the pyrochlore type, they have a lower symmetry. This was indicated in an early study[3], where the X-ray diffraction patterns for these compounds were obtained for the first time. The infrared spectra of the compounds $La_2Ti_2O_7$, $PrTi_2O_7$, and $Nd_2Ti_2O_7$ also illustrate the difference between their crystal structure and that of pyrochlore. However, the structures of these compounds were elucidated significantly later[50] when $La_2Ti_2O_7$ and $Nd_2Ti_2O_7$ single crystals were obtained. It was found that the crystals have a monoclinic structure with the space group $P2_1/m$; the lattice parameters are listed in Table 2.

Table 2. The unit cell parameters of $La_2Ti_2O_7$ and $Nd_2Ti_2O_7$.[50]

Compound	a, Å	b, Å	c, Å	β	V, Å^3
$La_2Ti_2O_7$	7.80±0.01	5.54±0.01	13.01±0.02	98°37′±10′	556
$Nd_2Ti_2O_7$	7.68±0.01	5.46±0.01	12.99±0.02	98°30′±10′	559

It has also been shown[50] that the above compounds are isomorphous with $Ca_2Nb_2O_7$ and that their lattice consists of slightly distorted perovskite blocks. However, these results required further confirmation, since the Weisenberg diagrams revealed twinning of the single crystals investigated. Subsequent studies[43,44] led to two different

interpretations. Thus the $La_2Ti_2O_7$ structure was interpreted[44] on the basis of orthorhombic symmetry; according to Gasperin's data[43], $La_2Ti_2O_7$ has a monoclinic structure close to the orthorhombic structure (and for this reason called by the authors pseudo-orthorhombic) with the space group $P2_1/m$ or $P2_1$. The latter structure can be regarded as consisting of TiO_6 octahedra joined together via their vertices. The presence of planes parallel to the (010) plane and dividing the structure into layers comprising four octahedra between which La atoms are accommodated is also typical.

Also of interest is a study[70] where it was noted that, since the crystal lattice parameters of pyrochlore vary linearly with the ionic radius, extrapolation can yield the parameters a_1 and a_2 which the compounds $La_2Ti_2O_7$ and $Nd_2Ti_2O_7$ would have had if their structure had been of the pyrochlore type. The results ($a_1 = 10.418$ Å, $V_1 = 565.4$ Å^3, and $a_2 = 10.286$ Å, $V_2 = 544$ Å^3) showed that under these conditions the volumes V_1 and V_2 are greater than for monoclinic symmetry. Hence the authors[70] concluded that heat treatment under pressure may promote the appearance of the monoclinic form of the compounds $R_2Ti_2O_7$, which are cubic under the usual conditions. The first experiments on $Sm_2Ti_2O_7$, carried out by the quenching method under pressure ($p = 54$ kbar, $t = 1390°$C), showed that the X-ray diffraction pattern obtained is no longer characteristic of pyrochlores, and may be interpreted on the basis of monoclinic or orthorhombic symmetry.

Table 3. The unit cell parameters of compounds of the type R_2TiO_5.

Compound	Structure	a, Å	b, Å	c, Å	β	Refs.
La_2TiO_5	orthorhombic	10.97	11.37	3.937	—	51
Nd_2TiO_5	orthorhombic	10.720	11.361	3.840	—	39
Sm_2TiO_5*	orthorhombic	10.59	3.792	11.351	—	9
Eu_2TiO_5*	monoclinic	15.82	5.34	15.76	92°29′	60
Gd_2TiO_5	monoclinic	15.75	5.32	15.73	87°34′	24, 60
Gd_2TiO_5	monoclinic	15.49	5.25	15.28	87°39′	19
Gd_2TiO_5	hexagonal	3.683	—	11.995	—	14
Gd_2TiO_5	orthorhombic	10.61	11.27	3.73	—	40
Dy_2TiO_5	monoclinic	15.56	5.26	15.35	87°38′	19, 24
Dy_2TiO_5	orthorhombic	10.49	11.26	3.70	—	40
Y_2TiO_5	monoclinic	15.75	5.32	15.73	87°34′	19
Y_2TiO_5	orthorhombic	10.35	3.70	11.25	—	41

*Sm_2TiO_5 and Eu_2TiO_5 were obtained in the study of the phase diagrams of R–O–Ti ternary systems.

Such studies appear promising for the synthesis of compounds of low symmetry with new properties (for example, ferroelectric properties), which the given compounds did not possess in the cubic phase. However, preliminary experiments for the heat treatment of $Dy_2Ti_2O_7$ and $Tb_2Ti_2O_7$ under pressure showed that the pyrochlore structures are fairly stable and for this reason the transition to the monoclinic form of compounds with lanthanide ionic radii smaller than $r_{Sm^{3+}}$ requires fairly high pressures and temperatures (in excess of 2000 °C and 70 kbar).

Studies in recent years[14–16,19–24,38–42,57,58] showed the presence in the R_2O_3–TiO_2 systems also of phases other than those described, namely compounds of the type R_2TiO_5 for the oxide ratio $TiO_2 : R_2O_3 = 1 : 1$. The first of these was obtained[11,24,29] for R = La, Gd, or Dy. Nowadays compounds of this type are known for R = La, Nd, Sm, Eu, Gd, Dy, Er, or Y.

The existence of two R_2TiO_5 modifications—the low-temperature orthorhombic modification (α) and the high-temperature hexagonal modification (β)—apparently created certain difficulties for the determination of the structure and because of this there was no unanimous view on this problem. The X-ray diffraction patterns of the compounds R_2TiO_5 were interpreted[24,60] on the basis of a monoclinic lattice, which was regarded as derived from the fluorite lattice. The unit cell parameters of compounds of the type R_2TiO_5 obtained hitherto are listed in Table 3.

The most detailed structural studies on compounds having the general formula R_2TiO_5 have been made in Refs. 38, 39, 41, and 51. Müller-Buschbaum and Scheunemann[39] examined the structure on the basis of an Nd_2TiO_5 single crystal. The unit cell contains four Nd_2TiO_5 formula units. Structures of this type have characteristic coordination numbers and coordination polyhedra made up of lanthanide and titanium atoms. The lanthanide atoms are surrounded by seven oxygen atoms ($n = 7$), six of which make up a distorted octahedron. A skeleton of octahedra joined together via their faces and nodes is formed, each two octahedra, located along the [001] face with $z = 1/4$ and $z = 3/4$, being joined via the seventh, common oxygen ion. This characteristic seventh ion constitutes simultaneously a vertex and is part of the base of a trigonal pyramid made up of oxygen ions around the Ti^{4+} ion. The same polyhedra as in the hexagonal form A of the pure sesquioxide Nd_2O_3 are distributed in the three-dimensional structure around the neodymium atom.

A coordination number of five, which is characteristic of Ti^{4+}, is observed only in the above compounds and in K_2TiO_5. The crystal structure of Nd_2TiO_5 is analogous to that adopted[41] for Y_2TiO_5. All other lanthanide titanates having the general formula R_2TiO_5 are also isomorphous with Y_2TiO_5[41,71] and their structures constitute a fairly rare example of the coexistence of 7- and 5-coordination of ions. The unusual 5-coordination for the titanium ion is also noted in a study[71], where the compounds R_2TiO_5 (R = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, or Y) were investigated by infrared and Raman spectroscopy. Two experimental features characteristic of these compounds were noted in particular[71]:

1. In the region of low frequencies (< 350 cm^{-1}) those corresponding to the absorption bands in the infrared spectrum and to the peaks in the Raman spectrum are correlated with the ionic radius of the lanthanide, i.e. as a rule are sensitive to the mass of the tervalent cations R^{3+}.

2. Sharp infrared absorption bands and the most intense peaks in the Raman spectrum are observed in the frequency range 775–875 cm^{-1}. These are unusually high frequencies; thus in compounds of the type β-Ba_2TiO_4 with 4-coordinate titanium the frequencies assigned to the vibrations of the TiO_4 polyhedra are in the range 690–750 cm^{-1}; in compounds with 6-coordination (Sr_2TiO_4) the frequencies are in the range 550–625 cm^{-1}. In order to account for the presence of peaks at such high frequencies in the R_2TiO_5 spectra, a comparison was made[71] with the infrared spectra of the compounds $KTiOPO_4$ and $RbTiOPO_4$ in which titanium atoms are surrounded by six oxygen atoms but one of the Ti–O bonds is shorter than the others. In these compounds the same infrared frequencies (775–850 cm^{-1}), associated with the Ti–O vibrations are observed. On the basis of this analogy, the author concluded that the vibrational frequencies in the R_2TiO_5 spectra, located

above 350 cm^{-1}, refer to the internal vibrations of the TiO_5 groups and that the highest-frequency peaks are due to the fact that one oxygen atom in the TiO_5 polyhedron differs structurally from the other four oxygen atoms. Because of this, one of the Ti–O distances is shorter than the others, which alters the vibration frequency associated with the TiO_5 group.

V. PROPERTIES OF LANTHANIDE TITANATES

The physicochemical properties of lanthanide titanates of type $R_2Ti_2O_7$ have been investigated in a number of studies. Table 5 presents the melting points, densities, thermal expansion coefficients α, refractive indices n, and the microhardness values H_μ of the compounds $R_2Ti_2O_7$, measured for both polycrystalline[36] and single-crystal[55] specimens. It shows that all the above characteristics as a rule increase with increasing atomic number of the elements. It has been stated[55] that the experimental densities of compounds of the pyrochlore type agree satisfactorily with the values estimated from the lattice parameter. We may note that, whereas the difference between the densities of single-crystal and polycrystalline materials is small, the microhardness of the single crystals obtained by Ershova et al.[55] is significantly higher than for polycrystalline compounds. The crystals also have a higher refractive index.

Table 4. Certain properties of compounds of the type $R_2Ti_2O_7$.

Compound	Colour	Density, g cm^{-3}		M.p., °C (Ref.36)	$10^6\alpha$, K^{-1} (Ref.36)*	n (Ref.55)	H_μ, kgf mm^{-2}	
		Ref.36	Ref.55				Ref.36	Ref.55
$La_2Ti_2O_7$	white	5.71	—	1650	9.46	—	400	—
$Pr_2Ti_2O_7$	green	—	5.73	1560	—	—	—	648
$Nd_2Ti_2O_7$	lilac	5.77	6.10	1650	9.80	—	—	712
$Sm_2Ti_2O_7$	white	6.06	6.20	1630	10.16	2.21	850	1103
$Eu_2Ti_2O_7$	white	—	6.29	1650	10.70	2.27	720	1104
$Gd_2Ti_2O_7$	white	6.41	6.50	1740	10.29	2.36	720	1114
$Tb_2Ti_2O_7$	cream	6.54	6.59	—	10.35	2.38	780	1122
$Dy_2Ti_2O_7$	white	6.52	6.76	1730	10.31	2.39	720	1152
$Ho_2Ti_2O_7$	cream	6.75	6.81	1820	10.25	2.41	660	1198
$Er_2Ti_2O_7$	pink	6.81	6.91	1780	10.66	2.47	850	1202
$Tm_2Ti_2O_7$	white	6.95	7.07	1820	10.41	2.48	1030	1232
$Yb_2Ti_2O_7$	white	7.12	7.21	1890	10.9	2.51	1140	1264
$Lu_2Ti_2O_7$	white	—	7.27	—	9.87	2.57	—	1293
$Y_2Ti_2O_7$	white	4.66	4.83	2000	10.46	2.34	—	1099

*In the temperature range 20–800°C.

There have been fairly numerous studies on the EPR spectra of lanthanide titanates with the pyrochlore structure[72,73], the luminescence and transmission spectra[74,75], the Mössbauer effect, and the Gol'danskii–Karyagin effect[76] in the Mössbauer spectra of compounds of the type $R_2Ti_2O_7$.[77–82] Thus the wavelength range in which the $Er_2Ti_2O_7$, $Yb_2Ti_2O_7$, $Gd_2Ti_2O_7$, and $La_2Ti_2O_7$ crystals are virtually transparent (0.3–15 μm) has been determined[75]. The characteristics of the quadrupole interaction and the spin–lattice relaxation in $Dy_2Ti_2O_7$ at temperatures $\leq 750°C$ have been published[77]. The isomer shift and the effective field at the Gd^{3+} nucleus in $Gd_2Ti_2O_7$ have been determined[78]. The study of $Gd_2Ti_2O_7$ and $Er_2Ti_2O_7$ [80–82] revealed a significant contribution of the Gol'danskii–Karyagin effect due to the asymmetry of the quadrupole doublets in the Mössbauer spectrum. These results indicate a considerable anisotropy of the vibrations of the lanthanide atoms in the titanate lattices. Thus the application of Mössbauer spectroscopy in the study of lanthanide titanates established their dynamic structures (i.e. the characteristics of various atomic motions in the molecules and crystals of substances in this class) and hence made it possible to supplement significantly the results of X-ray diffraction studies, which reveal the "static" structure of crystals[83].

Studies devoted to the magnetic and electrical properties of lanthanide titanates merit much attention.

1. Magnetic Properties

The study of the magnetic properties of the pyrochlore-type compounds $R_2Ti_2O_7$ (R = Gd, Tb, Dy, Ho, Er, Yb, or Nd) with a cubic structure showed that antiferromagnetic ordering takes place in many of them only at very low temperatures[84–89] ($T_N \simeq 1.5$ K).

It is clear from the standpoint of the crystal structure that the magnetic behaviour of the lanthanide ion in titanates with the pyrochlore structure must be similar to that observed in oxides[90] and lanthanide gallate garnets[91], where the closest distances between lanthanide ions are respectively 2.66 and 3.8 Å and the magnetic interaction is relatively weak (the Er–Er distance in $Er_2Ti_2O_7$ is approximately 3.562 Å).

The first measurements of the magnetic susceptibility as well as experiments on the adiabatic demagnetisation of certain compounds $R_2Ti_2O_7$ (R = Gd, Dy, Ho, or Er) with the pyrochlore structure were carried out by van Geuns[84]. In the experimental temperature range (2–80 K) all the compounds proved to be paramagnetic; above 8 K the magnetic susceptibility obeys satisfactorily the Curie–Weiss law with a Curie constant which agrees to within 10% with the theoretical value for the free ion. However, deviations from the Curie–Weiss law are observed for $Dy_2Ti_2O_7$ and $Gd_2Ti_2O_7$ below 8 K. Measurements on the magnetically diluted compound $Dy_{0.2}Y_{1.8}Ti_2O_7$ showed that in this case the deviations of the $\chi^{-1}(T)$ relation from linearity decrease and the Curie–Weiss law holds down to 2 K. This justifies the conclusion that the observed deviations arise mainly as a result of exchange interaction between lanthanide ions. It was shown[84] that the small Curie–Weiss constant and the relatively high ionic density make the compounds suitable for the attainment of low temperatures by the method of adiabatic demagnetisation. This stimulated a number of more detailed studies[88,92,93] on magnetisation and magnetic entropy as a function of temperature and external field.

Apart from the applied aspect described above, the interest in lanthanide titanates is due to the fact that, by virtue of their simple cubic structure they are convenient physical objects for testing various models of the theory of the magnetism of lanthanide compounds. In this connection mention should be made of a study[85] where the magnetic susceptibilities of $Dy_{0.2}Y_{1.8}Ti_2O_7$ and $Yb_2Ti_2O_7$ were examined theoretically. Measurements of the heat capacities of the double oxides $R_2Ti_2O_7$ (R = Dy, Er, or Yb) at ultralow temperatures are of special interest[86].

The principal data on the magnetic properties of the compounds $R_2Ti_2O_7$ (R = Gd, Tb, Dy, Ho, Er, Yb, or Nd), obtained in the above investigations and by Cashion et al.[87] and Mamsurova et al.,[89] are given below.

(a) $Dy_2Ti_2O_7$. According to Flood[88], $Dy_2Ti_2O_7$ passes to the antiferromagnetic state at $T_N = 1.4$ K, which agrees with $T_N = 1.35$ K found for single crystals[87]. The effective magnetic moment $\mu_{eff} = 9.6\ \mu_B$ obtained[88] is close to

$\mu_{eff} = g\sqrt{J(J+1)} = 10.63\ \mu_B$ for the free ion. However, it follows from the measurements of susceptibility at ultra-low temperatures[86] that χ decreases almost to zero when $T \to 0$. This indicates the anisotropy of the properties of $Dy_2Ti_2O_7$. Furthermore, the observed changes in entropy at low temperatures ($\Delta S_{magn} \simeq R \ln 2$) are inconsistent with the higher degeneracy (more than by a factor of 2) of the ground state[86].

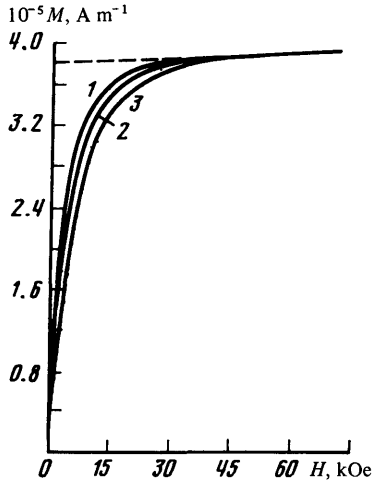


Figure 8. Dependence of the magnetisation of $Dy_2Ti_2O_7$ on the external field[88]; temperature (K): 1) 2.18; 2) 2.95; 3) 4.2.

The crystal field generated at the lattice sites occupied by lanthanide ions due to the 8 nearest oxygen ions is known[49,66] to have a predominantly axial symmetry. The deviation of the positions of the lanthanide ions from cubic symmetry is also greater than that in garnets[66], where the g-factor has been shown[91] to be significantly anisotropic, particularly for Dy and Er. Townsend and Crossley[85] calculated the corresponding parameters of the crystal field and obtained in this way the theoretical susceptibility curve for the magnetically dilute compound $Dy_{0.2}Y_{1.8}Ti_2O_7$ and compared it with experiment. This enabled them to conclude that the ground state of Dy^{3+} consists of a pure Kramers doublet with a projection of the overall moment $J_z = \pm 15/2$. For the pure state with $J_z = \pm 15/2$, there exists only one direction corresponding to easy magnetisation in the single-crystal material, which implies that $g_\perp = 0$ and $g_\parallel = 20$. It is then found that, for high values of J, the susceptibility of the powder is always close to the values for the free ion, since $J^2 \simeq J(J+1)$. However, the saturation magnetisation of the powder should be smaller than for the free ions. This was demonstrated by measuring the magnetisation in strong fields[88]. Fig. 8 illustrates the dependence of the magnetisation on the field strength for several temperatures[88]. The saturation magnetisation obtained is smaller by a factor of 2 than was expected for the isotropic case and agrees well with the fact that the ground state of the Dy^{3+} ion is represented by an orbital doublet: the experimental data presented in Fig. 8 yield $n_B = 9.4$ (where n_B is the number of Bohr magnetons per ion); on the other hand, if the ground state is represented by a pure doublet, then the theoretical values $n_B = g_\parallel J' = 10$. The small difference between these values arises apparently because the wave function for the ground state contains terms due to an admixture of excited levels (Van Vleck paramagnetism).

The absolute magnetic entropy was obtained in the same study[88] as a function of temperature and the external magnetic field. The results show that the compound $Dy_2Ti_2O_7$ can be used as the working substance in the magnetic cooling cycle in the temperature range between the boiling points of liquid hydrogen and liquid helium.

(b) $Yb_2Ti_2O_7$. Fig. 9 presents the temperature dependence of the reciprocal of the susceptibility for $Yb_2Ti_2O_7$ according to the results of Townsend and Crossley[85]. The curve exhibits a significant deviation from linearity, which the authors attribute to the influence of the crystal field. The ground state $^2F_{7/2}$ of the free Yb^{3+} ion is split by the cubic field into three levels Γ_7, Γ_8, and Γ_6. As a result of trigonal distortion, Γ_8 is split further into two Kramers doublets Γ_6 and Γ_7. The authors[85] showed that Γ_7 is the ground state. They calculated the crystal field parameters and the energy gaps $\Gamma_6 - \Gamma_7 = 1040$ cm^{-1} and $\Gamma_8 - \Gamma_7 = 530$ cm^{-1}. The theoretical magnetic susceptibility curves agree well with experiment (Fig. 9).

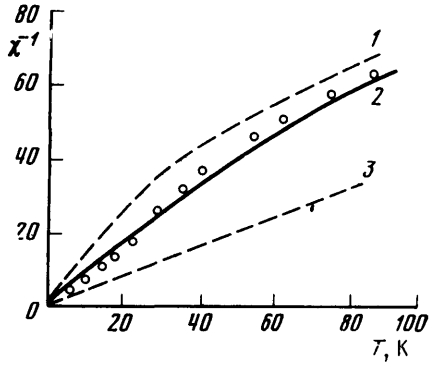


Figure 9. Temperature dependence of the reciprocal of the magnetic susceptibility of $Yb_2Ti_2O_7$;[85] the circles represent experimental points: 1) and 2) theoretical curves with different crystal field parameters; 3) free ion.

Certain parameters of the crystal field obtained[94] from the analysis of the Mössbauer spectra for ^{170}Yb in $Yb_2Ti_2O_7$ made it possible to explain the weak quadrupole interaction in this compound.

The heat capacity curve, illustrated in Fig. 10,[86] exhibits a singularity at 0.214 K, which apparently corresponds to the transition to the antiferromagnetic state. The observed entropy change $\Delta S/R = 0.693 = \ln 2$ corresponds to a Kramers doublet as the lowest state.

The exchange integrals $|J/k| = 1.2$–1.4 K (k is the Boltzmann constant), the nuclear contribution to the heat capacity, $C_{hfs}T^2/R = 0.00011K^2$, and the g-factors ($g = 2.1$–2.4) have been estimated[86].

(c) $Er_2Ti_2O_7$. According to Blote et al.,[86] the heat capacity of $Er_2Ti_2O_7$ exhibits a distinct λ-anomaly at T_N = 1.25 K. The entropy change determined from the heat capacity curves $\Delta S = 0.675R \simeq 0.97 \ln 2$. Consequently the singularity in the heat capacity is presumably due to long-range magnetic ordering (with a Kramers doublet as the ground state). The slope of the $\chi^{-1}(T)$ curve, measured by van Geuns[84] for powdered specimens, corresponds to the slope of the analogous curve for the free ion, while according to Blote et al.[86] the slope is smaller by a factor of approximately 3.5 over the limited temperature range 1.4–4 K. The latter may correspond to $g = 5.5$ if only the Kramers doublet is populated. van Geuns obtained a high Curie–Weiss constant $\theta = 22$ K, the high value of which cannot be due to magnetic interaction. Blote et al.[86] claim that this can be explained by assuming that the Er^{3+} ion has a doublet 10 cm^{-1} above the ground state; the combined effect of the two doublets then makes the susceptibility of the powdered specimen approximately the same as that of the free ions. Estimation of the exchange interaction integrals[86] yields $|J/k| = 0.56–0.63$ K.

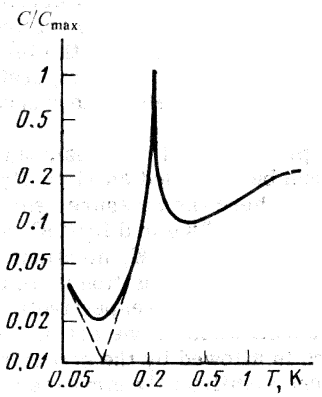


Figure 10. Temperature dependence of the heat capacity of $Yb_2Ti_2O_7$[86] (left-hand dashed line—nuclear contribution to the heat capacity).

(d) $Gd_2Ti_2O_7$. The splittings of the energy levels in the crystal field for the Gd^{3+} ion with the ground state $^8S_{7/2}$ ($L = 0$) are very small and the magnetic properties of the ion are presumably the same as those of the 8-fold degenerate ground state. Fig. 11 (curve *4*) shows that the susceptibility of $Gd_2Ti_2O_7$ is independent of temperature below 4 K.[87]

(e) $Ho_2Ti_2O_7$ and $Tb_2Ti_2O_7$. The Ho^{3+} and Tb^{3+} ions have an even number of $4f$ electrons. Because of this, their ground state is not a Kramers doublet but two singlets separated by a small gap. The magnitude of the gap enters directly into the expression for the magnetic susceptibility, determines T_N, etc. However, there are no detailed literature data for $Ho_2Ti_2O_7$ and $Tb_2Ti_2O_7$. Fig. 11 (curves *1* and *3*)[87] illustrates the $\chi(T)$ relations for these compounds. The susceptibility of $Ho_2Ti_2O_7$ follows a simple Curie law with $\chi = C/T$ and exhibits an antiferromagnetic transition at $T_N = 1.3$ K. The Curie constant C corresponds to the value for the free ion but can be accounted for (as for $Dy_2Ti_2O_7$) also by the non-Kramers pair discussed above, when $g_\parallel = 20$ and $g_\perp = 0$ (or $\langle J_z \rangle = \pm 8$).

(f) $Nd_2Ti_2O_7$. Neodymium dititanate belongs to the class of compounds for the magnetic properties of which there are still no literature data. As already mentioned, in contrast to the majority of compounds of the type $R_2Ti_2O_7$, $Nd_2Ti_2O_7$ has a monoclinic structure[50] (space group $P2_1/m$; $z = 4$).

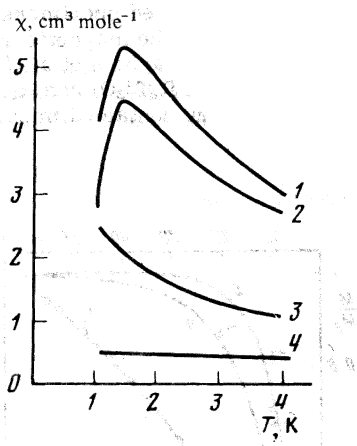


Figure 11. Temperature dependence of the magnetic susceptibilities of different lanthanide titanates: 1) $Ho_2Ti_2O_7$; 2) $Dy_2Ti_2O_7$; 3) $Tb_2Ti_2O_7$; 4) $Gd_2Ti_2O_7$.[87]

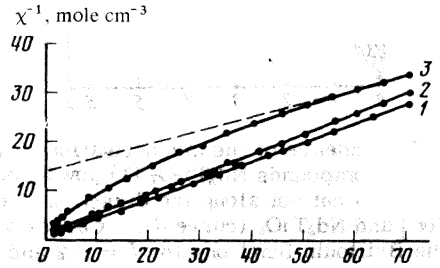


Figure 12. Temperature dependence of χ^{-1} of the compounds $Nd_2Ti_2O_7$ [1) for specimen cut out along the direction of easy magnetisation; 2) for powdered specimen] and Nd_2TiO_5 (curve *3*).

We measured the low-temperature susceptibility of $Nd_2Ti_2O_7$ (in the temperature range 1.6–70 K) and the magnetisation in the field of a superconducting solenoid (up to 55 kOe)[89]. Fig. 12 (curves *1* and *2*) shows that the compound remains paramagnetic up to 1.6 K. The Curie–Weiss law holds over the entire experimental temperature range with the parameters $C = 2.44$ $cm^3 K$ $mole^{-1}$ and $\theta = -3$ K. The value of C obtained yields $\mu_{eff} = 3.12\ \mu_B$ for the effective magnetic moment of Nd^{3+}, which is close to the value for the free ion.

It is noteworthy that the observed values of θ apparently reflect the influence of the crystal field on the orbital moment of $4f$ electrons rather than of the exchange interaction between Nd^{3+} ions. The tenfold degenerate level of the free Nd^{3+} ion is known to be split into five doublets in crystal fields whose symmetry is lower than cubic. Since the Curie–Weiss law holds for $Nd_2Ti_2O_7$ over the entire experimental temperature range, presumably the ground state of the Nd^{3+} ion in this compound (the Kramers doublet) is fairly remote from the nearest excited levels, which are not populated even at 70 K. In this case an effective moment $J' = 1/2$ and $g = \mu_{eff}/\sqrt{J(J+1)} = 3.6$ can be attributed to the Nd^{3+} ion in $Nd_2Ti_2O_7$.[89]

It is noteworthy that all the studies mentioned above were carried out using powdered specimens, which significantly restricts the scope of the magnetic measurements. An exception is the study of Cashion et al.,[87] who used for the investigation very small $R_2Ti_2O_7$ and R_2TiO_5 crystals, but, as already stated, they contained impurities.

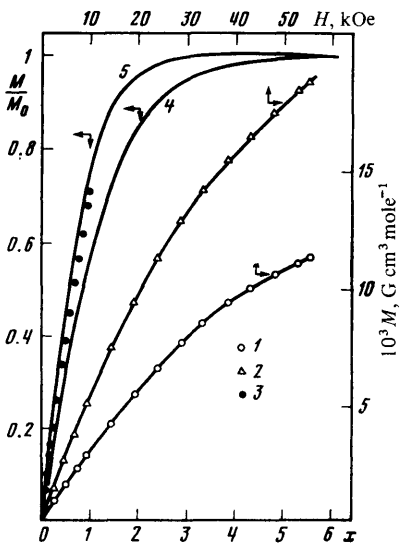


Figure 13. Dependence of the magnetisation on the external field for the compounds $Nd_2Ti_2O_7$ [1) powdered specimen; 2) specimen cut out along the direction of easy magnetisation] and Nd_2TiO_5 (curve *3*). Curves *4* and *5* represent the Brillouin functions for $J = 1/2$ and $J = 1$.

We attempted[89] to investigate a cylindrical $Nd_2Ti_2O_7$ specimen, consisting of small coalesced acicular single crystals, in which the crystallographic directions of all the crystals coincided. The susceptibility and the magnetisation of the specimens along this direction proved to be greater than for the powdered specimen. Although in the maximum field of 55 kOe the magnetisation does not reach saturation (Fig. 13), the nature of the $M(H)$ relations suggests that the saturation magnetisations for the two different $Nd_2Ti_2O_7$ specimens are different. Evidently, the anisotropy in $Nd_2Ti_2O_7$ is of a single-ion type and is manifested in the given case in terms of the anisotropy of the g-factor.

In the same study[89] measurements were made on a polycrystalline Nd_2TiO_5 specimen. Fig. 12 (curve *3*) shows that the Curie–Weiss law does not hold in this case, in contrast to $Nd_2Ti_2O_7$. The slope of the $\chi^{-1}(T)$ curve in the region of 60 K and above corresponds to $\mu_{eff} = 3.54\ \mu_B$, i.e. approaches the value for the free ion. Under these conditions, θ becomes greater than the usual value ($\theta = -45$ K). Since the substance remains paramagnetic down to 1.6 K, θ is evidently determined by the influence of the crystal field.

With decrease of temperature, the slope of the curve changes and $\mu_{eff} = 2.03\ \mu_B$ in the range 1.6–4.2 K. It is natural to suppose that at such low temperatures only the lowest Kramers doublet is populated; the effective value is then $J' = 1/2$ and $g = \mu_{eff}/\sqrt{J(J+1)} = 2.3$. This is confirmed by measurements of the magnetisation of Nd_2TiO_5 in fields up to 55 kOe. Fig. 13 presents the results of measurements as a plot of the relative magnetisation M/M_0 against $x = g\mu_B JH/kT$, where $T = 4.2$ K, $g = 2.3$, $J = 1/2$, and $M_0 = 2\,Ng\mu_B J = 12.84$ CGSM units $mole^{-1}$ (N is the Avogadro number). Evidently the points obtained lie closer to the theoretical Brillouin function of x for $J = 1/2$ and for $J = 1$.

Consequently in the compound Nd_2TiO_5, which has orthorhombic symmetry, the internal crystal field splits the tenfold degenerate ground state of the free Nd^{3+} ion in such a way that the distance between the levels is not as large as in $Nd_2Ti_2O_7$ and, when the temperature is raised from 1.6 to 60 K, all the sublevels of the ground multiplet are populated.

The magnetic properties of other lanthanide titanates of the type R_2TiO_5 can be regarded as virtually uninvestigated. Only one report[87], where the measurements of the magnetic susceptibilities of Gd_2TiO_5 and Dy_2TiO_5 are presented for the temperature range 1–4 K, mentions that the specimens apparently undergo a transition to an antiferromagnetic phase at 1.25 and 1.55 K respectively.

Isomorphous substitution of one set of magnetic atoms by another, which is allowed by the structure of the compounds R_2TiO_5, can significantly increase the phase transition temperature and can also alter other magnetic characteristics of the substance[95]. A study of the magnetic susceptibility of single-crystal $NdFeTiO_5$ in which some of the Nd^{3+} ions have been replaced by Fe^{3+} ions revealed the occurrence of antiferromagnetic ordering at $T_N = 18.5 \pm 0.5$ K. T_N is determined in this case by the cooperative ordering of the spin system of the Fe^{3+} ions. The Nd^{3+} ions remain paramagnetic below T_N, but their magnetic moments are polarised owing to interaction with the Fe^{3+} spin. The principal characteristics of the temperature dependence of the magnetic susceptibility can be explained on the hypothesis that there is interaction between the ordered spins of the Fe^{3+} ions and the electrons populating the lowest Kramers doublet in the Nd^{3+} ions[95].

2. Electrical Properties

The resistivities of all the lanthanide titanates, including scandium and yttrium titanates, were measured for the first time at room temperature and those of certain titanates ($La_2Ti_2O_7$, $Nd_2Ti_2O_7$, $Sm_2Ti_2O_7$, $Ho_2Ti_2O_7$, and $Er_2Ti_2O_7$) at a higher temperature (up to 1000°C) by Brixner[8] in 1964. The resistivity at room temperature was approximately $10^{12}\ \Omega$cm [the lower resistivity ($\sim 10^{10}\ \Omega$cm) obtained for three compounds, with cerium, praseodymium, and terbium, was explained by the author as due to the loss of oxygen by the specimens during heat treatment in an

inert atmosphere]. The order of magnitude of the resistivity apparently shows that ionic conduction, due to the diffusion of ions, predominates, which is characteristic of a defect pyrochlore structure[69]. On raising the temperature to 1000°C, the resistivity falls exponentially to 10^2 Ω cm (Fig. 14). Thus the compounds investigated are *p*-type semiconductors, which means that at high temperatures the electronic mechanism of conduction becomes dominant.

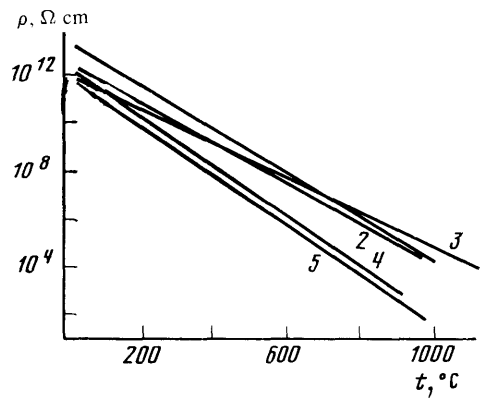


Figure 14. Temperature dependence of the electrical conductivities of lanthanide titanates: 1) $La_2Ti_2O_7$; 2) $Nd_2Ti_2O_7$; 3) $Ho_2Ti_2O_7$; 4) $Sm_2Ti_2O_7$; 5) $Er_2Ti_2O_7$.[8]

The temperature dependence of the dielectric constants of all the titanates has been measured[8]. The author notes the extremely high values of the constants ($\epsilon \simeq 30$–40) at room temperature. The measurement of the temperature dependence of ϵ was undertaken in the hope of observing ferroelectric properties in the compounds investigated. However, the measurements showed that the dielectric constant hardly changes with temperature below room temperature and increases somewhat when the temperature is raised further. The author[8] correctly attributes this increase of ϵ to the exponential decrease of the resistivity of the specimen and not to its ferroelectric behaviour.

The search for ferroelectric materials among complex oxides with a pyrochlore structure has been prosecuted for many years, apparently in connection with the discovery in 1952 of a low-temperature ferroelectric modification of the compound $Cd_2Nb_2O_7$,[1] which has the pyrochlore structure at room temperature. It was found that the properties of this compound differ from those of all other ferroelectrics and are so unusual that they attracted attention to the entire class of compounds of the pyrochlore type[2-4]. It might have been expected that other ferroelectrics with similar structure would have interesting properties. The existence in the pyrochlore-type structure of octahedra distributed in a specified manner and joined together via their vertices (this arrangement is most favourable for the manifestation of ferroelectric properties[2]) makes it very similar to a perovskite type structure, many representatives of which are typical ferroelectrics. After considering chains of oxygen tetrahedra in a pyrochlore type structure, Megaw[96] concluded that cadmium pyroniobate might also have ferroelectric properties.

Nevertheless $Cd_2Nb_2O_7$ is so far the only ferroelectric with the pyrochlore structure which has been investigated in detail, although broad maxima on the curves relating ϵ and tan δ to temperature have been observed for a number of pyrochlore compounds. According to the authors, they are associated with ferroelectric and antiferroelectric transitions[97,98]. Attempts to detect ferroelectricity in a series of lanthanide titanates with the pyrochlore structure were again undertaken in 1969.[7] However, measurements of the dielectric constants of $Sm_2Ti_2O_7$ and $Er_2Ti_2O_7$ in the range from room temperature to the helium temperature also failed to detect ferroelectric transitions.

The existence in the $R_2Ti_2O_7$ series of compounds with a symmetry lower than cubic (R = La, Nd, or Pr) stimulated further investigation of their dielectric properties[4,53]. Monoclinic crystals are known to belong to the class of polar crystals. Very careful studies enabled Nanamatsu et al.[5] to announce that lanthanum titanate ($La_2Ti_2O_7$) is a new ferroelectric with an extremely high Curie temperature, one of the highest among all known ferroelectrics. Similar properties were also discovered in an $Nd_2Ti_2O_7$ single crystal[4].

A hysteresis loop has been observed[4] in the curve relating the electric [dielectric?] shift to the field strength at room temperature in a strong electric field of approximately 300 kV cm^{-1}. The spontaneous polarisation and the coercive field were obtained from these measurements. Ferroelectric domains have been observed in $Nd_2Ti_2O_7$ single crystals when the latter were etched in boiling aqueous nitric acid. The crystals thus grown proved to consist of a single domain; pyroelectricity was clearly revealed along the *b* axis at room temperature and its polarity could be altered by applying to the specimen an electric field of 370 kV cm^{-1}.

Table 5. Ferroelectric, electro-optical, and piezoelectric properties of $La_2Ti_2O_7$ and $Nd_2Ti_2O_7$ single crystals.

Parameter	$La_2Ti_2O_7$ (Ref.5)	$Nd_2Ti_2O_7$ (Ref.4)
Size of single crystal	d = 5 mm, l = 50 mm	d = 5 mm, l = 30 mm
Melting point, °C	1790	1800
Crystal lattice	monoclinic	monoclinic
Space group	C_2^2—$P2_1$	C_2^2—$P2_1$
Density, g cm^{-3}	5.79	6.08
Curie temperature, °C	1500	>1500
Spontaneous polarisation, μC cm^{-2}	5	9
Coercive field, kV cm^{-1}	45	200
Dielectric constants (at a frequency of 1 kHz)		
ϵ_{11}	52	31
ϵ_{22}	62	43
ϵ_{33}	42	47
Quality coefficient $1/\epsilon V_\pi^2$, V^{-2}	$27 \cdot 10^{-7}$	$24 \cdot 10^{-9}$
Electromechanical coupling factor k_{22}	0.29	0.15
Piezoelectric constants d_{22}	$16 \cdot 10^{-12}$	$6.5 \cdot 10^{-12}$
Elasticity constant s_{22}	$5.5 \cdot 10^{-12}$	$4.8 \cdot 10^{-12}$

Measurement of the temperature dependence of the dielectric constant of $Nd_2Ti_2O_7$ revealed no anomalies in the range from room temperature to 1500°C. The authors[4] therefore suggested that the Curie point of this specimen lies above 1500°C.

The data obtained by Nanamatsu and coworkers[4,5] are presented in Table 5. The investigations led to the conclusion that both compounds ($La_2Ti_2O_7$ and $Nd_2Ti_2O_7$) are

ferroelectrics with high coercive fields at room temperature and high Curie points; the observed excellent electro-optical and piezoelectric properties of these compounds may be useful for their practical applications.

Similar studies have not so far been made on compounds of the type R_2TiO_5, although they should apparently exhibit dielectric properties of the same type. This was pointed out by the authors of an early investigation [11], who believed that the similarity of the dielectric properties of the compounds $La_2O_3.TiO_2$ and $La_2O_3.2TiO_2$ follows from plots of the temperature variation of tan δ and (Fig. 15).

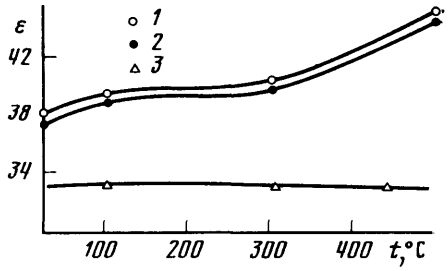


Figure 15. Temperature dependence of the dielectric constants ε (at a frequency of 1 MHz) of three binary compounds [11]: 1) $La_2O_3.TiO_2$; 2) $La_2O_3.2TiO_2$; 3) $2La_2O_3.9TiO_2$.

VI. EXAMPLES OF PRACTICAL APPLICATIONS

The possibility of using lanthanide titanates as dielectrics has been discussed in the literature for a long time. As early as 1946, mixtures of lanthanide oxides, including lanthanum and titanium oxides, were patented [99] as suitable for use in condensers as a dielectric layer with a weak temperature dependence of the dielectric constant.

The development of radioengineering industry and the requirement for new materials with optimal parameters stimulated a number of recent studies [100-106], designed to discover ceramic dielectric compositions suitable for various condensers. The dielectric properties of $La_2Ti_2O_7$ proved to be extremely useful for such purposes. Thus a new dielectric ceramic having the composition $(La_2Ti_2O_7)_{1-\alpha}(Sr_2Nb_2O_7)\alpha$, where $0 < \alpha \leq 0.85$, has been reported [100,101] as suitable for condensers with temperature compensation. This ceramic has a high value of ε, low dielectric losses, and a weak temperature dependence of the dielectric constant. It has been mentioned in almost all the investigations that the addition of different amounts of $La_2Ti_2O_7$, up to 1.2 mole %, to ceramic materials of different composition significantly decreases the temperature dependence of the dielectric constant and improves the properties of the materials.

The ceramic containing 35–50 mole % $PbTiO_3$, 25–35 mole % $SrTiO_3$, 4.5–15 mole % $CaTiO_3$, 3–20 mole % Bi_2O_3, 0.5–20 mole % TiO_2, and 4–12 mole % $La_2Ti_2O_7$ is a material which can be used successfully in a high-voltage condenser [103]. Its dielectric constant is unusually high ($\epsilon = 1850$) and the breakdown potential is 14 kV mm^{-1}.

It has been shown [107,108] that $La_2Ti_2O_7$ can also be used in condensers for the preparation of transistors on thin films of complex structure. A special method for the manufacture of such films has been developed [108].

Yet another aspect of the applications of lanthanide titanates is associated with $Eu_2Ti_2O_7$. Europium is an element suitable for the control of excess reactivity in nuclear reactors because it has a high thermal neutron absorption cross-section and resistance to damage by radiation [109]. The oxide Eu_2O_3 can be used for the same purpose. However, tests for resistance to corrosion carried out in water at 250°C and a pressure of 45.5 atm [110] showed that the best results are obtained when europium and titanium are combined ($Fu_2Ti_2O_7$). The chemical stability of this material, its properties, and behaviour under intense incident radiation have been discussed [109].

The development of laser technology has been accompanied by continuously growing requirements for laser crystals. A high thermal stability and chemical purity, optical transparency, and mechanical strength are qualities characteristic of lanthanide titanates which may prove useful in laser research. Analysis of the transmission spectra quoted [75] for $Er_2Ti_2O_7$, $Yb_2Ti_2O_7$, $Gd_2Ti_2O_7$, and $La_2Ti_2O_7$ demonstrated the suitability of these materials as matrices for various lanthanide additives in the preparation of crystals for infrared lasers.

As already mentioned above, the compounds under consideration can be used successfully as the working substances in the attainment of low temperatures by adiabatic demagnetisation.

Presumably further studies on lanthanide titanates (especially R_2TiO_5) may significantly supplement our knowledge of their physicochemical properties and hence extend significantly the limits of their practical applications.

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