Translated from *Uspekhi Khimii*, **57**, 367-384 (1988) U.D.C. 546.651/669

Lanthanide Oxide Sulphides

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A systematic account is given of the methods of preparation of oxide sulphides having the composition Ln_2O_2S (where Ln = lanthanide, Sc, or Y) in the form of polycrystalline materials, single crystals, thin films, and ceramics. The crystal-chemical, thermal, thermodynamic properties of the oxide sulphides are considered.
The bibliography includes 117 references.

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I. INTRODUCTION

Compounds having the composition Ln_2O_2S, where Ln = lanthanide, Sc, or Y, are known for all the lanthanides without exception and also for scandium and yttrium. They occupy an intermediate position between the oxides and sulphides of the corresponding elements. All these groups of compounds are structurally related as regards either their crystal lattices or individual structural fragments. The practical aspects of the application of lanthanide oxide sulphides have attracted in the first place the continued attention of investigators and a broad spectrum of materials based on them have already been created: powders (ceramics), single crystals, thin layers, and films.

The polycrystalline oxide sulphides or solid solutions based on them, in the first place lanthanum oxide sulphide activated with Nd, Er, Tm, and Yb, are highly effective anti-Stokes phosphors (with green and blue glow) and can be used, in the form of phosphor coatings emitting in the IR part of the spectrum, to make light emitting diodes, digital and alphanumeric indicators and indicator panels, and colour television. In the USSR and other countries, methods have been developed for the growing of single crystals of lanthanum oxide sulphide activated with Nd, Er, and Yb. Combined studies on such single crystals—structural, optical, mechanical, and spectroscopic (the luminescence characteristics of laser emission)—have demonstrated their likely usefulness by the creation of low-threshold microlasers and unified light diodes. However, the difficulties in the growing of single crystals of a high quality have not as yet been overcome.

This review is devoted to the consideration of the questions concening the formation of point defects in the oxide sulphide and their thermal and thermodynamic properties, which will fill the existing gap in the literature.

II. METHODS OF SYNTHESIS

Apparently the first lanthanide oxide sulphide obtained was lanthanum oxide sulphide. Subsequently extensive patent literature appeared on the methods of synthesis of the oxide sulphides and phosphors based on them.

Studies by investigators in many countries, especially France, the USA, Finland, the USSR, etc., have been devoted to the methods of preparation of the oxide sulphides and have found extensive applications in the technology of phosphors. The methods of synthesis are distinguished by wide variety. All the known procedures reduce in essence to two schemes which are chemically fundamentally different. In the first scheme, the sulphur is introduced into the initial sulphur-free oxygen compound of the lanthanide by some kind of sulphur-containing reagent, as a rule a sulphide or elemental sulphur. In the second scheme, the initial sulphur-containing lanthanide compound is reduced, oxidised, or decomposed to the oxide sulphide. We shall consider the existing methods of synthesis of oxide sulphides in conformity with the schematic arrangement which we have proposed.

1. The Introduction of Sulphur into Lanthanide Oxide Compounds

The introduction of sulphide sulphur can be achieved by treatment with various compounds, using elemental sulphur,[1-6] hydrogen sulphide,[2,3,7-10] carbon disulphide,[11] sulphides,[5,7] ammonium or sodium thiocyanate,[5] and thioacetamide[11] (Table 1).

In the general form, the chemical reactions take place in accordance with the scheme

$$Ln_2O_3+RS\rightarrow Ln_2O_2S+RO\,,$$

where R is the group of the "sulphiding" agent. Depending on the conditions and the reagents, one of the variants of the solid-phase, liquid-phase, or gas-phase syntheses is achieved.

When elemental sulphur is used, lanthanide oxides are treated with its vapour in an inert medium in one or two stages.[1-6] In the latter case, the synthesis is carried out initially at low temperatures (400–450 °C), which is then followed by annealing at 500–800 °C (Table 1). Oxide carbonates, oxalates, formates, etc. can be used instead of the oxide.[1]

When sulphur is introduced with the aid of carbon disulphide, it is also possible to obtain oxide sulphides, but these not only contain admixtures of substances which have failed to react but are also contaminated with carbon.[11-13] The introduction of sulphur by hydrogen sulphide in a stream of argon (nitrogen) with added water vapour is carried out at higher temperatures (1100–1150 °C)[1-3,8,9] and, in the case of CeO_2, at 1300 °C.[3]

The introduction of sulphur by gaseous reagents, which takes place at the solid–gas interface, leads to the appearance of a sulphide sulphur concentration gradient in the

bulk of the oxide sulphide grain, to its non-uniform content in particles of different size, and also to the formation of non-stoichiometric phases.

Table 1. Preparation of the oxide sulphides by the "sulphiding" method.

Initial compound	"Sulphiding" agent	Side products	t °C	τ, h	Medium	Refs.
Ln_2O_3	S	Ln_xS_y	1050—1120	1—2	Ar	[1]
Ln_2O_3[a]	S (excess)	Ln_xS_y	400—450; 500—800	1—2	inert	[2—4]
$Ln_2(C_2O_4)_3$, $Ln_2O_2CO_3$	S (excess)	Ln_xS_y	700	—	inert	[1]
Y_2O_3	S (excess)	Y_xS_y	950—1000	100	inert	[5]
Eu_2O_3+EuS	S (excess)	Eu_xS_y	600	7	inert	[6]
Ln_2O_3[b]	H_2S	H_2O	1000—1100	—	Ar (95%)	[1, 2]
Ln_2O_3[c]	H_2S	H_2O	550—600	—	—	[7]
$Ln_2O_2CO_3$	H_2S	H_2O, CO_x	500—800	4—5	H_2O (5%)	[8]
Ln_2O_3	H_2S	LnS_x, H_2O	1150±10	1.5	N_2, H_2O	[9]
Ln_2O_3[d]	H_2S	H_2O, LnS_x	850—1050	12—40	—	[10]
CeO_2	H_2S	S, H_2O	1300	—	—	[3]
Ln_2O_3	CS_2	C, CO	750—800	2—8	—	[11]
La_2O_3[e]	CS_2	C, CO_x, COS, S	600	4	He	[12]
Y_2O_3	CS_2	C, CO, Y_xS_y	1000	0.5	—	[13]
Ln_2O_3[f]	S+Na_2CO_3	Na_2S_{2+x}, CO_2	1100	1	—	[14—19]
Ln_2O_3[g]	Na_2SO_3	Na_2SO_4	1100	1	inert	[20]
Y_2O_3	S+NaCNS	Na_2S, CO_x	750	0.5	—	[5]
Ln_2O_3	CH_3CSNH_2 (excess)	CO_x, H_2O	1200	4—6	—	[11]
Ln_2O_3	Ln_2S_3 (excess)	Ln_2S_3	1350	3	vacuum	[7, 23]
Dy_2O_3[a]	Dy_2S_3	—	1300; 1600	5 3	$p < 0.1$ Pa	[21]
Sc_2O_3	Sc_2S_3 (excess)	Sc_2S_3	1500	4	—	[24]
Y_2O_3	Y_2S_3	Y_2S_3	1000	100	vacuum	[5]

Notation: t is the temperature and τ the duration of the synthesis. [a] The synthesis is carried out in two stages. [b] The method is used in industry. [c] The temperature of the synthesis of Ce_2O_2S is 500 °C. [d] Ln = Gd—Lu or Y; the temperature and the duration of the synthesis depend on the nature of Ln. [e] The yield of the oxide sulphide is 35%. [f] The temperature of the synthesis of Lu_2O_2S is 780 °C. [g] The yields of lanthanum, praseodymium, neodymium, samarium, and europium oxide sulphides are 95—98%; Ce_2O_2S and Pm_2O_2S were not investigated.

The degree of conversion increases significantly when the synthesis is performed in the melt of the "sulphiding" agent. A mixture of the lanthanide oxide with sulphur and sodium carbonate is heated at 1100 °C.[14—19] The reaction begins with the formation of sodium polysulphides from sodium carbonate and sulphur. These polysulphides melt and then introduce the sulphur into the lanthanide oxide with formation of the oxide sulphide. An advantage of the method is the evolution of carbon dioxide on decomposition of sodium carbonate, the dioxide protecting the oxide sulphide against oxidation. The method of introducing sulphur into oxides by sodium sulphite in an inert medium is closely related to the above procedure.[20] At high temperatures, sodium sulphite disproportionates to the sulphate and the sulphide, the melt of the last compound reacting with the lanthanide oxide. The maximum yield of the oxide sulphide (88—95%) is obtained at 1100 °C, after 1 h, and for the ratio $Na_2SO_3 : Ln_2O_3 = 4 : 1$. The reactivity of the oxide in the "sulphiding" reaction depends on the position of the metal in the series of lanthanides. Manashirov and Semikhova[20] divided the oxides into three groups in terms of their reactivities: the maximum reactivity is shown by the oxides of elements ranging from lanthanum to gadolinium, which form oxide sulphides at 1100 °C; ytterbium, lutetium, cerium, and yttrium oxides, which form appreciable smounts of oxide sulphide only at 1350 °C, have been assigned to the second group; the oxides of the remaining lanthanides produce a mixture of the oxide sulphide and the oxide which failed to react at 1100 °C.

The oxide sulphides are also obtained by the sealed tube method, the oxides being heated in an excess of thioacetamide at 1200 °C.[11] In the solid phase, the "sulphiding" agent is as a rule the sulphide of the same lanthanide.[5,7,21—24] The mixture of pressed oxide and sulphide, with 20% excess of the latter, is sintered for a long time at 1300—1500 °C in a medium protecting from oxidation (*in vacuo*). The oxide sulphides obtained by this method must also be freed from the excess sulphide. The oxide sulphide having the composition $Ce_4O_4S_3$, namely $Ce_2^{3+}Ce_2^{4+}O_4S_3$, in which the cation has a mixed valence, can be obtained by the sealed tube method in which sulphur is introduced into CeO_2 by the Ce_2S_3 + S mixture at 550—600 °C.[22] Analysis of the method based on the introduction of sulphur into the oxygen compound of the lanthanide shows that the oxide sulphides formed are as a rule contaminated and that they must be subjected to additional purification in order to remove the initial compound which failed to react, or side products.

2. The Reduction of Sulphates and Sulphites

A widely used method of synthesis of the oxide sulphides involves the reduction of lanthanide sulphates, oxide sulphates, or sulphites with hydrogen,[25—33] carbon monoxide,[34—42] or natural gas[29] (Table 2). When sulphates are used, oxide sulphates are formed initially and are then reduced in accordance with the scheme

$$Ln_2O_2SO_4+4CO \rightarrow Ln_2O_2S+4CO_2.$$

If the lanthanide can exhibit an oxidation state of +2, then the sulphate is reduced consecutively: initially to $LnSO_4$, according to data for $Eu_2(SO_4)_3$,[37] then to $Ln_2O_2SO_4$, and finally to Ln_2O_2S. The reduction can be carried out either by the pure reductant or by its mixture with an inert carrier (argon, nitrogen). During the synthesis, the sulphur

Table 2. Preparation of the oxide sulphides by reducing sulphates and sulphites.

Initial compound	Reductant	Side products	t, °C	τ, h	Refs.
$Ln_2(SO_4)_3$	CO	S, CO_2	500—650	—	[34—37]
$Ln_2(SO_4)_3$	H_2	S, H_2O	800	—	[25]
$Ln_2(SO_4)_3$	H_2+N_2(1:4)	S, H_2O	800	0.5	[26]
$Ln_2(SO_4)_3$	H_2+Ar(He)	S, H_2O	500—1000	0.5—2	[27]
$Ln_2(SO_4)_3$	H_2	S, H_2O	600—700	1	[28, 29]
$Ln_2O_2SO_4$	H_2	H_2O	750	—	[25, 31]
$Ln_2O_2SO_4$	CO	CO_2	900—1050	—	[37]
$Ln_2O_2SO_4$	H_2+H_2S	H_2O	1000	2	[38]
$Ln_2O_2SO_4$+$(NH_4)_2CO$	H_2+Ar(He)	NH_3, H_2O	—	—	[33]
$Gd_2O_2SO_4$	H_2+Ar(96%)	H_2O	—	—	[30]
$Ln_2(SO_3)_3$[a]	H_2	S, H_2O	600—700	1	[29]
$Ln_2(SO_3)_3$	CO	LnS_x, CO_2	700—830	1	[38—40]
$Eu_2(SO_3)_3$	CO	EuS, CO_2	650	—	[41]
$Ln_2(SO_3)_3nH_2O$[b]	H_2S	LnS_x	460—630	1	[42]

[a] Natural gas (550—650 °C) was also used as the reductant. [b] Eu_2O_2S is not formed under these conditions.

oxides are reduced to elemental sulphur. An advantage of the method considered is the high rate of reaction and the relatively low temperatures of the synthesis, particularly when sulphites are used (Table 2). A single-phase product not requiring additional purification is then formed. Evidently the method can be applied in a continuous process. When the nitrogen–hydrogen mixture is used, there is no harmful waste.

3. The Oxidation of the Sulphides

The formation of oxide sulphides has been observed in the oxidation of lanthanide sulphides in air.[6,43–47] The partial oxidation of Ln_2S_3 by treatment with a mixture of water vapour and air leads to the formation of a mixture of the oxide sulphide with the sulphide and the oxide, but, at a rigorously fixed temperature, it has been possible to obtained the stoichiometric lanthanum oxide sulphide by the method of vapour phase hydrolysis.[48] The formation of oxide sulphides has been established in the oxidation under relatively mild conditions of thin films of LnS or Ln_2S_3.[46,47] The oxide sulphides are also formed *in vacuo* or in an inert medium if there is an admixture of oxygen[21,46–49] (Table 3). The formation of the oxide sulphides in the oxidation of the sulphides with sulphur(IV) dioxide[31] and carbon dioxide[4,12,50] has been noted.

Table 3. Preparation of oxide sulphides by oxidising the sulphides.

Sulphide	Oxidant and medium	Side products	t, °C	τ, h	Refs.
La_2S_3, Gd_2S_3, Y_2S_3	SO_2	—	—	—	[31]
La_2S_3	H_2O, gas	—	650–680	1	[48]
La_2S_3, LaS_2	air	SO_2	640, 620	—	[43]
La_2S_3	CO_2	S, CO	630–790	—	[12]
La_2S_3	CO_2	S, CO	1200	2	[50]
La_2S_3, Pr_2S_3, Nd_2S_3, Y_2S_3[a]	CO_2		⩾600	—	[4]
Dy_2S_3	O_2+Ar	Dy_2O_3	800–1100	—	[21]
Tm_2S_3	vacuum (10^{-3} Pa) and admixture of O_2	Tm_2O_3	430	—	[49]
EuS	air	Eu_xO_y	300–600		[6, 44, 45]
EuS	air	Eu_xO_y	660	12	[10]
CeS[b], TmS, YbS	vacuum (admixture of O_2) or air	Ln_xO_y	330	[c]	[46, 47]

[a] The sulphides of the yttrium subgroup elements are oxidised to the oxides.
[b] The intermediate $Ce_2O_2S_2$ is formed in the oxidation of CeS.
[c] Prolonged heating.

A special method of synthesis of the oxide sulphides having a non-stoichiometric composition has been proposed.[51,52] In the thermal decomposition of the thiocarbamide complexes of lanthanide acetates and propionates in an inert medium, the thiocarbamide group rearranges to the thiocyanate group and oxide sulphides having the compositions $Ln_2O_{2.6}S_{0.4}$ and $Ln_2O_{2.4}S_{0.6}$ are formed at 300–335 °C. The stoichiometric oxide sulphides are produced when homogenised mixtures of the metal carboxylate and thiocarbamide, taken in proportions of 1:3, are heated for 1 h at 300–320 °C. The product, which is contaminated with carbon, must be heated in a stream of dry CO_2 at 600–650 °C.

Thin films of the oxide sulphides, for example, Sm_2O_2S, are formed as a result of the deposition of $(CH_3)_4C_6H_{10}Sm$ + S from the gas phase at 700 °C onto a SiC support.[53] Ceramic specimens of the oxide sulphides can be obtained by heating pressed Ln_2O_2S powders at 700–1300 °C and a pressure of $(9.8–19.8) \times 10^4$ kPa for 1–5 h.[19]

Apparently lanthanum oxide sulphide was the first compound of this kind to be obtained in the single crystal state.[54] The greatest advances in this field have been achieved at the end of the 1970's and the beginning of the 1980's.[24,55–60] Different versions of the method of direct recrystallisation from solution in the melt (the Bridgman–Stockburger, Czochralski, etc. methods) are used to obtain the single crystal, the procedure involving the creation in the crucible of an inert gas counterpressure (with argon or an argon–hydrogen mixture at a pressure of 300–1500 kPa).

4. Mixed Oxide Sulphides

Oxide sulphides containing two and more lanthanides have been known for a fairly long time and are obtained by the same methods as the oxide sulphides of the individual lanthanides. However, during the last decade there has been much interest in the mixed oxide sulphides containing, apart from the traditional lanthanide, also another element, as a rule a *d* or *p* element, whose chalcogenides are used to a greater or lesser extent to prepare semiconducting materials.

The methods of synthesis of such mixed oxide sulphides are based on the familiar procedures for the preparation of "simple" compounds.[61] Mixed lanthanide oxide sulphides containing Cu(I), Ag(I), Ga, In, Ge(IV), Sn(IV), Pb(II), As(III), Sb(III), Bi(III), Cr(III), and V(III) as the second element have been synthesised hitherto.[62,63]

III. CRYSTAL-CHEMICAL PROPERTIES

1. Crystal Structure

Compounds having the general formula $(LnO)_nX$, containing the lanthanide and oxygen (Ln = lanthanide, X = oxygen, chalcogenide, halide, carbonate, orthoborate, etc. ions), have a common feature involving the presence in the structure of the $(LnO)_2^{2+}$ "complex ion", first considered by Caro.[64] This complex has a tetrahedral structure. The oxygen atom is at the centre of the tetrahedron in the sp^3-hybridised state and the corners of the tetrahedron are occupied by lanthanide ions. However, the "complex ion" cannot be identified in all the compounds containing a lanthanide and oxygen. Kuz'micheva et al.[65] specified a series of conditions for the presence or absence of such an ion in the compounds $(LnY)_2X$. The main one is the existence in the structure of different crystallographic positions for the X and Y atoms.

By combining with one another, the $(Ln_4O)_n$ tetrahedra form layers. Laruelle[66] noted that two structures of the layer are possible (Fig.1): a trigonal structure in which the triangular base of each tetrahedron is parallel to the layer, and a tetragonal structure in which the orthogonal edges of the tetrahedron are located in the planes bounding the layer. Thus the entire wide variety of the structural types of the lanthanide oxide chalcogenides is ensured by different types of alternation of the anionic lattices with layers of the $(Ln_4O)_n$ tetrahedra oriented either in accordance with the trigonal law, as happens in La_2O_2S, or in accordance with the tetragonal law, which obtains in Nd_2O_2Te. The different structures arise as a result of the formation of a superstructure, monoclinic or orthorhombic distortions, and also displacements.

A relation which makes it possible to determine the symmetry of the tetrahedral layers constituting the basis of a

particular compound has been derived[65] from the close packing principles:

$$0.78 < \frac{r + R_t}{r + R_o} < 0.96 ,$$

where r is the ionic radius of the lanthanide for a coordination number of 7 and R_t and R_o are the oxygen radii for coordination numbers 4 and 6 respectively.

If the ratio of the sums of the radii is less than 0.78, compounds of the type $(LnO)_2X$ crystallise in structural types based on the tetragonal symmetry of the layer; if it is in the range 0.78–0.96, then they are based on trigonal symmetry, and if the ratio is greater than 0.96, then the "complex ion" cannot be identified in the compound containing a lanthanide and oxygen.

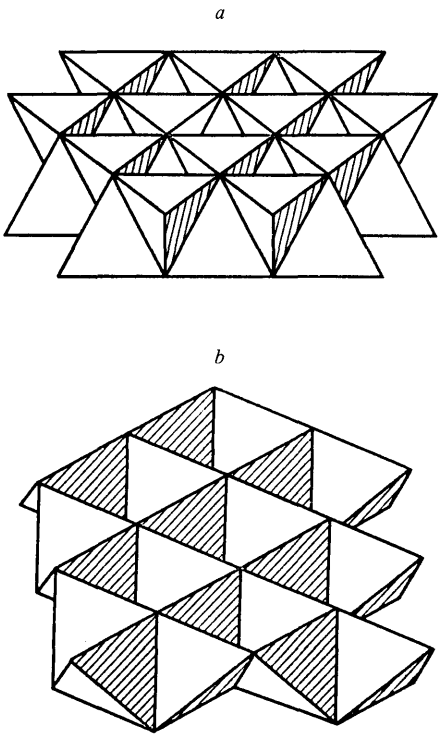


Figure 1. Trigonal (*a*) and tetragonal (*b*) construction of the $(LnO)_n^{n+}$ layer in the La_2O_2S and Nd_2O_2Te structure respectively.[62]

The structure of the lanthanide oxide sulphides having the composition Ln_2O_2S is based on a tetrahedral layer with trigonal symmetry and they are all isostructural for the entire series of lanthanide metals.[17] The structure of La_2O_2S can be derived from that of Ce_2O_3 by replacing an oxygen atom in the octahedral environment by a sulphur atom.[67] Fig. 2 presents projections of the La_2O_2S structure onto the xy and yz basal plane and also the coordination polyhedra around the La atoms.

Investigators have frequently attempted to refine the structure of Ln_2O_2S. One of such refinements has been carried out by means of the X-ray diffraction analysis of La_2O_2S : Nd single crystals, obtained by Czochralski's method,[55] on an autodiffractometer.[64] Polycrystalline Ho_2O_2S [69] and Nd_2O_2S [70] have been investigated by neutron diffraction at 300 and 4 K respectively. The thermal and positional parameters were refined as in the previous study. The large error in the determination of the thermal isotropic factors or even their negative values in the case of Nd_2O_2S can be explained by the presence in the specimen of a second phase, namely $Nd_2O_2S_2$:[70] no explanation has been found for Ho_2O_2S.[69] An attempt has been made to refine the multiplicity of the positions of sulphur in Ho_2O_2S.[70] The desirability to refine the populations of the different positions by sulphur atoms was justified by the possibility of the partial substitution of sulphur by oxygen. It was found that the population exceeds the multiplicity [number?] of the positions occupied, which can be in no way accounted for by the substitution of sulphur by oxygen. Nevertheless the refinement of the sulphur content made it possible to reduce somewhat the R factor.

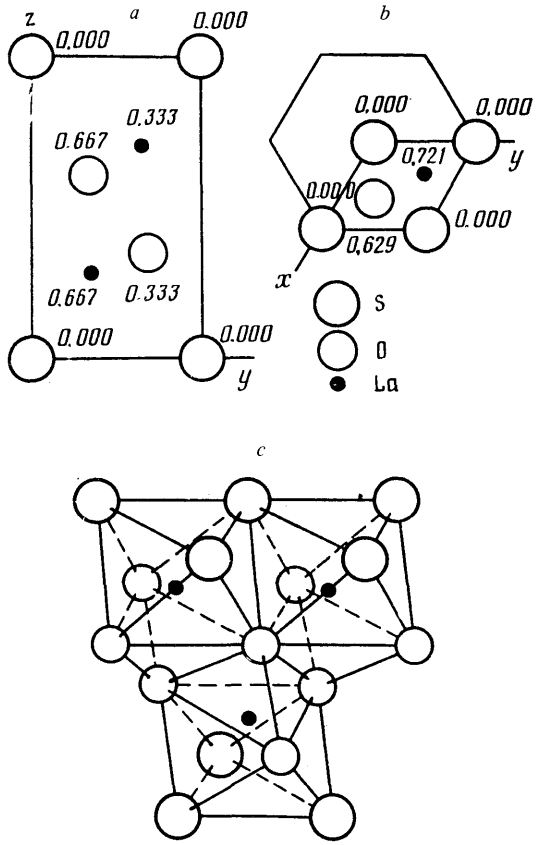


Figure 2. Projection of the La_2O_2S structure onto the yz (*a*) and xy (*b*) planes and the interlinking of the polyhedra around the La atoms (*c*). The numbers indicate the height along the $x(z)$ axis.

The structures of La_2O_2S : Ln single crystals, obtained by the modified Stockburger–Bridgman method,[57] have been investigated[71,72] on an autodiffractometer. According to the X-ray diffraction data, the crystals have a deficiency of sulphur and the metal, while the population of the oxygen sites is excessive.[71] Allowance for the partial incorporation

of sulphur in the oxygen sublattice and for the incorporation of oxygen in the sulphur sublattice (on the assumption that the sites are filled to the maximum extent) made it possible to reduce the *R* factor and to obtain crystal-chemically acceptable formulae of the compounds.[72] In the calculation of the difference electron density, a maximum was observed for the 0 0 1/2 site. This region of "concentrated" electron density was interpreted as interstitial atoms of neutral sulphur, occupying approximately 5% of these positions. However, one cannot rule out the possibility that lanthanum ions (or the ions of another lanthanide) are located at a low concentration in these positions.† These results were confirmed by the study of La_2O_2S : Ln single crystals by the chemical and neutron activation methods and by hydrostatic weighing.[72]

Thus crystal-chemical formula of lanthanum oxide sulphide can be written in the general form

$$La_{2-x}[\ ]_xO_{2-y}[\ ]_yS_{1-z}[\ ]_z(S_w^0)$$

where [ ] denotes vacancies here and henceforth. The formation of the principal point defects in La_2O_2S can be described by the following equation (in terms of the Kröger–Wink notation[73]):

(a) Schottky disordering reaction;

$$0 \rightleftarrows 2V_{La}^{\cdot\cdot\cdot} + 2V_O^{\cdot\cdot} + V_S^{\cdot\cdot}.$$

(b) Frenkel' disordering reaction:

$$La_{La}^x + V_i^x \rightleftarrows La_i^{\cdot\cdot\cdot} + V_{La}^{\cdot\cdot\cdot},$$

$$S_S^x + V_i^x \rightleftarrows S_i^x + V_S^x.$$

(c) Interfacial reactions at the crystal–vapour interface:

$$S_S^x \rightleftarrows 0.5S_2(gas) + V_S^{\cdot\cdot} + 2e^1,$$

$$O_O^x \rightleftarrows 0.5O_2(gas) + V_O^{\cdot\cdot} + 2e^1.$$

(d) Antistructural defects or atoms at "foreign" sites:

$$S^x + V_O^x \rightleftarrows S_O^x,$$

$$O^x + V_S^x \rightleftarrows O_S^x.$$

In the equations the dots, primes, and crosses denote positive and negative charges and neutral atoms respectively.

In principle there is a possibility of the formation of partly ionised or neutral defects[74] (for example, apart from the $V_S^{\cdot\cdot}$, $V_O^{\cdot\cdot}$, and $V_{La}^{\prime\prime\prime}$ forms, the vacancies can exist as $V_{La}^{\times}$, $V_{La}^{\prime\prime}$, $V_{La}^{\prime}$, $V_S^{\times}$, $V_S^{\cdot}$, $V_O^{\times}$, and $V_O^{\cdot}$). In this case the equations for defect formation presented here are supplemented by others. It has been shown[75,76] that, under the influence of pressure, the lanthanum oxide sulphide specimens change colour: at a low pressure, the colour of the specimens becomes pink, i.e. a colour centre, the so called *F*-centre $(V_S^{\cdot}, e')^{\times}$, is formed.

The results obtained for the defect formation have served as the basis of the mechanisms of diffusion in lanthanum oxide sulphide# and also of a high-speed method for the determination of the composition and the extent of defect formation according to X-ray diffraction data.§

2. The Region of Homogeneity

The La–O–S ternary system has not so far been fully investigated. The phase regions and the phase crystallisation conditions are unknown. Only the liquidus line for the compositions of the La_2S_3–La_2O_3 quasi-binary section (Fig.3),[77] having two maxima, has been determined. One of the maxima corresponds to La_2O_2S with a melting point of 2080°, which agrees well with the value found previously (2070 °C).[54] The second maximum corresponds to the composition La_2OS_2, which melts at 1960 °C.

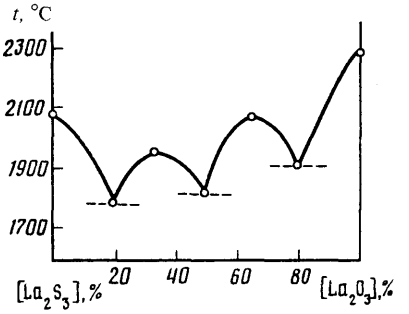


Figure 3. The liquidus in the La_2S_3–La_2O_3 system.[77]

In a study of the La_2S_3–La_2O_3 system,[78] the specimens were obtained by the method inovlving the solid-phase sintering of lanthanum sesquioxide and sesquisulphide *in vacuo* or in an atmosphere of argon (pressure 1–2 atm) at 1100–1200 °C for 4 h. A broad region corresponding to the existence of the lanthanum oxide sulphide phase having the composition

$$La_{2\pm x}O_{2\pm y}S_{1\pm z}$$

was established from the X-ray diffraction data. In the region of homogeneity, the plots of the variation of the lattice periods (Figs.4*a* and 4*b*) have a point of inflection corresponding to the composition La_2O_2S. The decrease in the periods on passing from La_2O_2S to La_2O_3 can be associated both with the subtraction of sulphur and metal via the

$$La_{2-x\cdot 2/3}[\ ]_{2x}O_2S_{1-x}[\ ]_x,$$

mechanism and with the substitution of sulphur by oxygen: $La_2O_2(S_{1-x}O_x)$. In the composition range La_2O_2S–La_2S_3, the decrease in the lattice period can be explained by the subtraction of oxygen and the metal, i.e.

$$La_{2-x\cdot 2/3}[\ ]_{x\cdot 2/3}O_{2-x}[\ ]_xS,$$

and also by the substitution of oxygen by sulphur, i.e. $La_2(O_{2-x}S_x)S$. The type of the solid solutions was established by measuring the density of the test specimens. Its variation within the limits of the region of homogeneity corresponds exactly to the substitution mechanism (Fig.4*c*). The composition $La_2O_{2.14}O_{0.86}$ corresponds to the boundary of the region of homogeneity on the La_2O_3 side, while the composition $La_2O_{1.71}S_{1.29}$ (1100 °C, 0.1 Pa) corresponds to the boundary on the La_2S_3 side (Fig.4*a*). At 1200 °C, the boundary specimens have the compositions $La_2O_{1.81}S_{1.18}$ and $La_2O_{2.09}S_{0.91}$ (Fig.4*b*), but one can hardly speak of a narrowing of the region of homogeneity with increase in temperature, because the results obtained vary within the limits of the accuracy of the phase analysis. Furthermore, there are

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†See G.M.Kuz'micheva, I.V.Perepelkin, N.V.Porotnikov, and D.S.Kholodnyi, Zhur.Neorg.Khim., 1985, **30**, 2981 [Russ.J.Inorg.Chem., 1985(11)].

#See G.P.Borodulenko, A.A.Eliseev, G.M.Kuz'micheva, et al., Zhur.Neorg.Khim., 1986, **31**, 567 [Russ.J.Inorg. Chem., 1986(3)].

§See G.M.Kuz'micheva, I.V.Perepelkin, and A.A.Eliseev, Zhur.Neorg.Khim., 1986, **31**, 2527 [Russ.J.Inorg.Chem., 1986(10)].

no grounds for the assumption that the defect-free crystal lattice with fully occupied atomic sites corresponds to the composition La_2O_2S.

Analysis of studies on the Ln–S–O systems, where Ln ≠ La, can also be of definite interest.[21,104] One of these has been devoted to the investigation of the Dy–S–O system in the region of homogeneity of dysprosium oxide sulphide.[21] Homogeneous specimens of dysprosium oxide sulphide having the general formula $Dy_2O_{2+x}S_{1+x}$ were synthesised by heating in a vacuum furnace (p < 0.1 Pa) mixtures of Dy_2O_3 and Dy_2S_3 at 1300 °C for 5 h and at 1600 °C for 3 h. The region of homogeneity in the temperature range 1300–1600 °C (for quenched specimens) hardly varies and extends from 19 (in the case of $Dy_2O_{2.05}S_{0.95}$) to 23 at.% of sulphur ($Dy_2O_{1.85}S_{1.15}$). The variation of only the period c was observed in this composition range, while the period a remains constant within the limits of the error of the determination (±0.003 Å). This character of the variation of the lattice parameter of Dy_2O_2S with the sulphur content indicates the formation of substitutional solid solutions in the concentration range indicated.

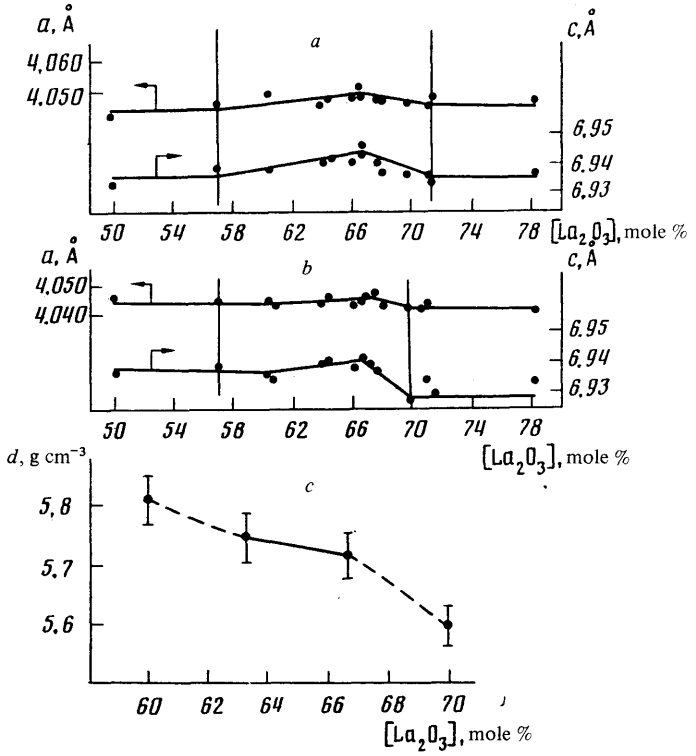


Figure 4. Variation of the lattice periods (a, b) and of the densities (c) of lanthanum oxide sulphide at 1100 °C (a) and 1200 °C (b and c) *in vacuo* along the La_2S_3–La_2O_3 section.[78]

IV. SOLID SOLUTIONS IN THE Ln'_2O_2S–Ln''_2O_2S SYSTEM

A number of studies[8,29,40,79–81] have been devoted to solid solutions of the type $(Ln', Ln'')_2O_2S$. In particular the La_2O_2S–Ln_2O_2S systems, where Ln = Nd, Sm, Eu, Gd, Dy, Yb, Lu, or Y, have been examined.[40] Total miscibility has been observed only in the La_2O_2S–Nd_2O_2S and La_2O_2S–Sm_2O_2S systems, while in the remaining systems there are two-phase regions. The possibility of the existence of solid solutions is determined by the ratio of the ionic radii: a continuous series of solid solutions are formed for

$$[R(La^{3+}) - R(Ln^{3+})]/R(Ln^{+3}) < 9\%$$

Apart from the $(La, Ln)_2O_2S$ systems, Leskela[38] also investigated systems based on yttrium oxide sulphide: Y_2O_2S–Nd_2O_2S and Y_2O_2S–Eu_2O_2S (Fig.5). The above dimensional criterion is valid also in this case: in the former system ($\Delta R/R$ = 9.2%), a limited miscibility is observed, while in the latter ($\Delta R/R$ = 5.2%) the miscibility is complete. The specimens for the investigations were prepared by the reduction of coprecipitated lanthanide sulphates with carbon monoxide at 800 °C.

It has been stated[40] that the limit of the two-phase regions as well as the lattice period depend on the method of preparation of the $(Ln', Ln'')_2O_2S$ powders. Indeed the miscibility in the La_2O_2S–Y_2O_2S specimens obtained by "sulphiding" in a stream of $0.2H_2S + 0.8N_2$ (1200–1250 °C) a homogeneous mixture of coprecipitated lanthanide oxide powders[79] is somewhat different from that in the analogous system described by Leskela and Ninisto.[40] This difference cannot be explained by the different temperature of the synthesis, because the two-phase region does not become narrower on raising the temperature from 800 °C [40] to 1200 °C [79] and its width remains unchanged, the region being merely displaced towards La_2O_2S. On the other hand, the lattice periods of individual oxide sulphides in the La_2O_2S–Gd_2O_2S system, found in the above two investigations,[40,79] are identical, although a different value has been obtained for the La_2O_2S–Y_2O_2S system.

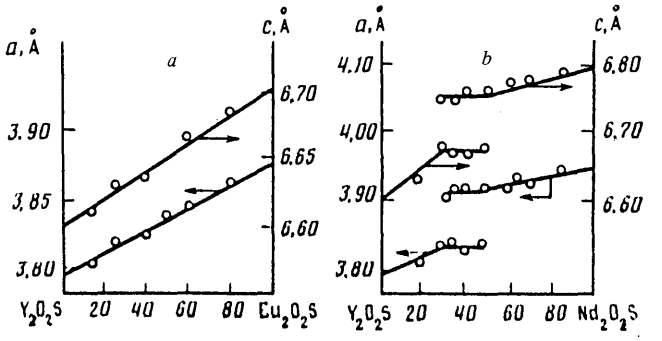


Figure 5. Variation of the lattice periods as a function of the composition of the Y_2O_2S–Eu_2O_2S (a) and Y_2O_2S–Nd_2O_2S (b) systems.[40]

Completely different results for the miscibility of the oxide sulphides have been published in a study[88] where the existence of a continuous series of solid solutions in the La_2O_2S–Ln_2O_2S systems (Ln = Pr, Eu, or Yb) was discovered. The $(La, Pr)_2O_2S$ solid solutions were obtained by oxidising a mixture of the polysulphides in a stream of $H_2 + H_2O$ (3 vol.% H_2O) for 3–4 h at 520 °C. The $(La, Eu)_2O_2S$ and $(La, Yb)_2O_2S$ specimens were obtained by introducing sulphur in the liquid phase into the corresponding solid solutions of the oxide carbonates (500–700 °C, 4–5 h). The lattice periods of the individual oxide sulphides in these systems, quoted in the above investigations,[40,79] are the same within the limits of experimental error and the temperatures of the synthesis are similar.

An attempt has been made[82] to calculate the binodal curve for the decomposition of the solid solutions in the La_2O_2S–

Ln_2O_2S systems by the method of Urusov and co-workers[83,84] in order to elucidate the influence of various factors on the width of the region of homogeneity. The calculation is based on the principle that the Gibbs free energy of mixing tends to a minimum, which also determines the state of equilibrium in the isomorphous mixture; the vibrational and configurational entropies were taken into account. This calculation made it possible to explain the discrepancies between the limits of miscibility in the La_2O_2S–Ln_2O_2S systems and to demonstrate the marked dependence of the limits of the region of homogeneity on the method of preparation of the solid solutions, which determines the common structural unit and the degree of defectiveness of the initial components.

V. THERMAL AND THERMODYNAMIC PROPERTIES

The oxide sulphides Ln_2O_2S occupy an intermediate position, as regards composition, in the Ln_2S_3–Ln_2O_2S–Ln_2O_3 series. They differ from the sulphides by a greater thermal stability in an oxidising medium but are greatly inferior to the oxides in this respect. The thermal stability of the oxide sulphides in an inert medium (argon) has been determined for both the individual and the erbium-, ytterbium-, and neodymium-activated lanthanum oxide sulphide.[85,86] Lanthanum oxide sulphide is stable up to 1450 °C, but, starting from 1500 °C, when the specimens have been maintained for 1 h under the given conditions, the stoichiometry of the oxide sulphide phase changes. At higher temperatures the oxide sulphide evaporates and dissociates; the composition of the gas phase is complex and has not been established unambiguously. Fused lanthanum oxide sulphide is gradually depleted in sulphur and its loss reaches 30% after the melt has been allowed to stand for 5 h.[55]

The thermal properties of the oxide sulphides on heating in an oxidising medium (air) have been studied by many investigators.[30,81,87–93] It has been established by various methods of thermal analysis (thermogravimetric, derivatographic measurements, and differential thermal analysis) that the oxide sulphides are oxidised by air directly to the oxide sulphates $Ln_2O_2SO_4$. However, it has been observed by the derivatographic method that praseodymium, europium, and gadolinium oxide sulphides are oxidised in air in two stages.[90,92,93] The oxidation of Gd_2O_2S in the first stage is accompanied by the formation of an intermediate oxide sulphite phase having the composition $Gd_2O_2SO_3$. Presumably, the oxide sulphite is formed initially as an intermediate in the oxidation of praseodymium and europium oxide sulphides. The oxide sulphites of the above metals are stable within a narrow temperature range and are oxidised to the oxide sulphates at a higher rate than the oxide sulphides.[92] The fact that the formation of the oxide sulphites has not been observed in all the cases investigated confirms their thermal instability. In pure oxygen, the oxidation of oxide sulphides is rapid. The temperatures of the onset of the activation of Ln_2O_2S and the temperature ranges where these compounds are oxidised to the oxide sulphates differ by 80–100 °K in the above studies, which can be explained by the different purities of the specimens, the different conditions in their preparation (disc or powder), and the different methods of investigation, i.e. the specific features of the study of the heterogeneous system under non-equilibrium conditions.

The temperature ranges of the stability and of the onset of oxidation of lanthanide oxide sulphides are arranged systematically in Table 4. Overall, the polycrystalline lanthanide oxide sulphides are stable in air up to 450–500 °C, but Ce_2O_2S begins to oxidise already at temperatures above 180 °C.[7] The rate of oxidation at the beginning of the process is low, but, above a certain temperature limit which depends on the type of the lanthanide, it increases sharply. The temperature of the onset of oxidation increases in the sequence La_2O_2S–Lu_2O_2S, Y_2O_2S, occupying an intermediate position in the middle of the series. The oxide sulphates, the final sulphur-containing products of the oxidation of the oxide sulphides, are more stable; their stability decreases in the sequence La–Lu, Y occupying the position after Dy. When the rate of heating is reduced from 10 to 1 K min^{-1}, the temperatures of the onset of the oxidation of La_2O_2S and Y_2O_2S decrease from 765–770° to 620–640 °C. The stability of the oxide sulphides is influenced by the degree of crystallinity of the specimens. After they have been kept in an inert medium (nitrogen), the temperature of the onset of oxidation increases by ~100 K and the rate of oxidation falls.

Table 4. The oxidation temperatures of the lanthanide oxide sulphides.

Oxide sulphide	t_o, °C	$t_{0.5}$, °C (Refs.88, 89)	Oxide sulphide	t_o, °C	$t_{0.5}$, °C (Refs.88, 89)
La	500–800 [90]	765	Gd	700–1000 [30]	—
La	510–910 [32]	—	Gd	450–630 [90]	—
La	650–680 [86]	—	Tb	620–690 [90]	710
La	960[a] [60]	—	Dy	—	740
Ce	>180 [7]; 300–600 [91]	—	Ho	—	800
Pr	530–650 [90]	715	Er	—	835
Nd	610–680 [90]	720	Tm	—	840
Sm	630–930 [11]	800	Yb	—	790
Sm	650–780 [90]	—	Lu	635–850 [32]	770
Eu	300–680 [45]	750	Y	595–950 [32]	790
Eu	380–580 [81]	—	Y	750–950 [18]	—
Eu	500–570 [90]	—	Y	990[a] [60]	—
Gd	470–855 [32]	800			

Notation. t_o is the temperature of the onset of oxidation or the range of oxidation temperatures, $t_{0.5}$ is the temperature corresponding to the oxidation of 50% of the oxide sulphide.

[a] Single crystal.

Note. The numbers in square brackets denote references (Ed. of Translation).

Table 5. The oxidation temperatures of the solid solutions $(La, Y)_2O_2S$ and $(Eu, Y)_2O_2S$.[81]

Composition[a]	t_o, °C	t_d, °C	Composition[b]	t_o, °C	t_d, °C
Eu_2O_2S	510	1280	La_2O_2S	640	1470
$(Eu_{0.8}Y_{0.2})_2O_2S$	535	1270	$(La_{0.8}Y_{0.2})_2O_2S$	705	1445
$(Eu_{0.6}Y_{0.4})_2O_2S$	550	1255	$(La_{0.6}Y_{0.4})_2O_2S$	740 and 790[c]	1250; 1430
$(Eu_{0.4}Y_{0.6})_2O_2S$	560	1200	$(La_{0.4}Y_{0.6})_2O_2S$	660 and 720[c]	1220; 1350
$(Eu_{0.25}Y_{0.75})_2O_2S$	585	1185	$(La_{0.2}Y_{0.8})_2O_2S$	780	1190
Y_2O_2S	720	1170	Y_2O_2S	720	1170

Notation: t_o is the temperature of the onset of oxidation and t_d the decomposition temperature of the oxide sulphate.

[a] The composition of a continuous solid solution is quoted.
[b] The composition of a solid solution with limited miscibility is quoted.
[c] Two-stage oxidation.

The thermal oxidation of solid oxide sulphide solutions depends on the type of the solid solution (Table 5). The continuous solid solutions (Eu_2O_2S–Y_2O_2S) are oxidised as individual compounds. The temperature of the onset of

oxidation then diminishes with increase in the content of the less stable component and the temperature limits of the stability of the oxidised phase increase, i.e. a dependence of the thermal stability on the mole fractions of the components of the pseudobinary system is observed. The solid solutions with limited miscibility (when the difference between the ionic radii of the lanthanide is greater than 10%) are oxidised to the oxide sulphates in two stages and the oxide sulphate phases also decompose into two stages.

In view of the instability of the oxide sulphides in oxidising and inert media at elevated temperatures, the determination of their melting points involves considerable experimental difficulties. The melting points of many oxide sulphides are therefore either unknown or have been determined with inadequate accuracy. The melting points indicated in the literature (Table 6) indicate, with the apparent exception of the melting point of La_2O_2S, the temperature range of the fusion of oxide sulphates rather than characterising the individual compounds.

Table 6. The melting points of the oxide sulphides.

Ln	M.p., °C	Refs.	Ln	M.p., °C	Refs.
Y	2120	[95]	Nd	1990	[96]
La	2070±30	[54]	Sm	1980	[96]
La	2080	[77]	Gd	>2000	[54]
La	1940	[96]			
Ce	2000±200	[3]			
Ce	1950	[95]			

The phase equilibria in the oxide sulphide systems have been studied only for the La–S–O system.[77,94] The equilibrium compositions of the La_2O_3(B), LaS_2, La_2S_3, $La_2O_2SO_4$, La_2O_2S, and $La_2O_2S_2$ phases coexisting at 800 °C have been established[94] (Fig.6). These data confirm the formation of La_2O_2S, detected previously in a study of the T–x section of the diagram for the La_2S_3–La_2O_3 system.[77] The above studies[77,94] are at present the only fundamental investigations which have been made on the phase equilibria in the oxide sulphide systems.

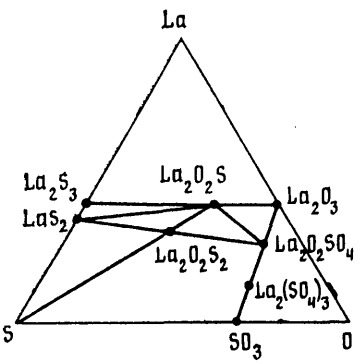


Figure 6. Isothermal section through the phase diagram for the La–S–O system (at 1073 K).[94]

The knowledge of the thermodynamic properties makes it possible to determine the conditions under which perfect oxide sulphide single crystals can be grown, for example, from their melts. Since the melts dissociate with evolution of gases which also contain elemental sulphur, the thermodynamic parameters are essential for calculations of the equilibrium pressure of the gas phase over the melt.

In an experimental study of the thermochemical properties of the oxide sulphides, it has been established that,[93,97–99] in a sulphuric acid solution of cerium(IV) sulphate, the oxidation proceeds in accordance with the equation

$$Ln_2O_2S(cryst.) + Ce(SO_4)_2(soln) + H_2SO_4(soln) \rightarrow$$
$$Ln_2(SO_4)_3(soln) + Ce_2(SO_4)_3(soln) + S_{orthorhomb} + H_2O(soln).$$

The enthalpies of these reactions have been measured by calorimetric methods and the standard enthalpies of formation of lanthanum, praseodymium, neodymium, and samarium oxide sulphates have been determined. The enthalpies of formation of europium and gadolinium oxide sulphates listed in Table 7 were calculated from the enthalpies of solution of the compounds in aqueous hydrochloric acid saturated with hydrogen sulphide (Table 7). The calculated enthalpies of formation of the oxide sulphides[100,101] differ from the experimental values by 85–100 kJ mol^{-1}. Consequently the theoretically deduced probable dissociation reactions of La_2O_2S [102] and the excess pressure of the gas phase over the melt necessary in order to be able to grow single crystals must be regarded as approximate.

Table 7. Thermodynamic functions of the oxide sulphides calculated from literature data.[93,97–99,104–110,114,116,117]

Compound	$-\Delta_fH^0$(298.15 K), kJ mol^{-1}	S^0(298.15 K)[a], J mol^{-1} K^{-1}	Δ_fG^0[b], kJ mol^{-1} (T, K)
La_2O_2S	1660.5±7.6	33.8	1538.7 (298 K)
	—	32.9	—
	—	34.8	—
Ce_2O_2S	1423.0±12	33.8	1423±12.6 (1072 K)
	1770.7±63 (1410 K)	34.4	1301.5 (1410 K)
Pr_2O_2S	1639.7±21	41.1	1425.1±62.8 (1072 K)
	—	34.2	1414.2±18.8 (1072 K)
	—	—	1514.9 (298 K)
Nd_2O_2S	1646.9±21	40.6	1523.3 (298 K)
	—	34.1	
Sm_2O_2S	1642.6±9.5	39.0	1517.9 (298 K)
	—	34.0	—
Eu_2O_2S	1469.0±8.9	38.4	1338.9 (298 K)
Gd_2O_2S	1644.9±4.0	38.4	1520.2 (298 K)
Y_2O_2S	—	30.2; 27.1; 28.8	1482.4±12.6 (1068 K); 1493.7±84 (1068 K)
Sc_2O_2S	—	21.3	—

[a] Approximate entropies obtained by different workers.
[b] The adjustment of the values of Δ_fH^0(298.15 K) and $\Delta_fG^0(T, K)$ for self-consistency is impossible owing to the lack of the temperature variation of the heat capacities of Ln_2O_2S and $Ln_2O_2SO_4$; the calculation of Δ_fH^0(298.15 K) from the temperature variation of $\Delta_fG^0(T, K)$ is also impossible for the same reason.

A tensimetric study of the CeO_x–CO–SO_2 equilibrium[103] and of the Eu_2O_3–H_2S–H_2–CO system[10] made it possible to calculate for the reactions

$$2CeO_2(cryst.) + 4CO(gas) + SO_2(gas) \rightarrow Ce_2O_2S(cryst.) + 4CO_2(gas)$$
(900–1400 °C)
$$4EuS(cryst.) + 2O_2(gas) \rightarrow 2Eu_2O_2S(cryst.) + S_2(gas)\ (900°).$$

the equilibrium pressures of the gaseous components and the Gibbs free energies of formation of cerium and europium oxide sulphides, which are also listed in Table 7.

The oxidation of the oxide sulphides in accordance with the equations

$$Ln_2O_2S(cryst.) + 2O_2(gas) \rightarrow Ln_2O_2SO_4(cryst.),\ Ln = Ce, Y;$$

$$Ln_2O_2S(cryst.) + 0.5O_2(gas) + 2Ag(cryst.) \rightarrow Ln_2O_3(cryst.) + Ag_2S(cryst.),\ Ln = La, Nd\text{-}Dy,$$

has been studied thermodynamically by an e.m.f. method using an oxygen ion solid electrolyte based on zirconium oxide.[105–110] The temperature dependence of the Gibbs free energy of the first of the above reactions has been found. The thermodynamic properties of the oxide sulphides (Table 7) and their enthalpies of oxidation (Table 8) were calculated by the present authors from the relations obtained. The values found made it possible to plot thermodynamic diagrams for the coexistence of the oxide, sulphide, and oxide sulphide phases[111–115] as a function of the partial pressures of O_2 and S_2 (Fig.7).

Table 8. The enthalpies of the oxidation of the oxide sulphides via the reactions $0.5\ Ln_2O_2S(cryst.) + O_2(gas) \rightarrow 0.5Ln_2O_2SO_4(cryst.)$.

Ln	ΔT, K	T_{av}, K	$\Delta H^0(T_{av}, K)$	$\Delta G^0(T_{av}, K)$
La	940—1250	1095	457±1.5	287±57
La	1100—1500	—	459.84	—
La	1190—1510	1350	—	477.7±3.8
Pr	1100—1400	1250	447.12	—
Nd	930—1200	1065	—	480.4±0.6[b]
Nd	1170—1400	1455	—	755±5
Sm	1050—1370	1160	453.44	—
Eu	1020—1320	1170	447.0	—
Gd	1000—1280	1140	445.57	908.5±6.5[c]
Tb	1020—1200	1110	453.48	—
Dy	1040—1180	1110	445.74	—
Ho	1000—1400	1250	446.9[a]	—
Er	1000—1400	1250	446.2[a]	—
Tm	1000—1400	1250	445.4[a]	—
Yb	1000—1400	1250	444.6[a]	—
Lu	1000—1400	1250	443.9[a]	—
Y	1190—1500	1345	—	1108.9±5.8

[a] Estimated quantities.
[b] At 1285 K.
[c] At 1380 K.

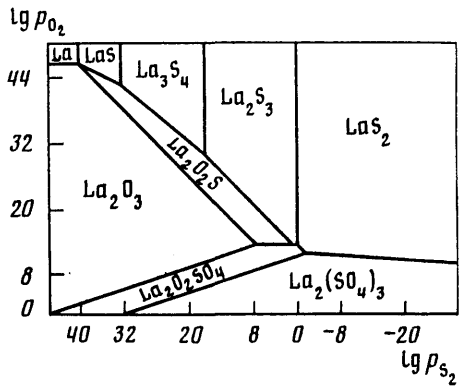


Figure 7. Isothermal section through the phase diagram for the La–S–O system (at 1100 K).

The standard entropies of the oxide sulphides have been estimated in a number of studies.[93,97,116,117] The values obtained have been used to calculate standard thermodynamic functions (Table 7) and, in particular, the Gibbs free energies, from which the equilibrium constants and the equilibrium vapour pressures of sulphur necessary for the selection of optimum conditions for the growing of perfect single crystals were calculated.

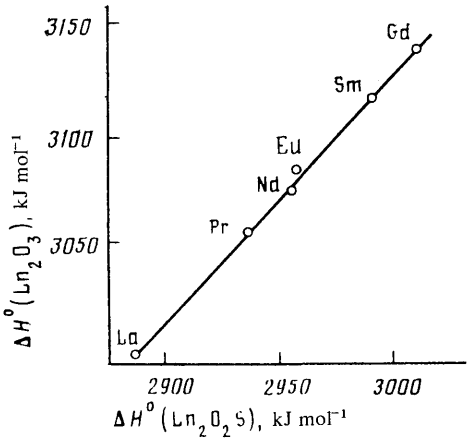


Figure 8. Relation between the crystal lattice energies of the lanthanide oxides and oxide sulphides.

Comparison of the thermodynamic functions of the oxide sulphides, sulphides, and oxides shows that the energies of formation of the compounds increase in the sequence Ln_2S_3–Ln_2O_2S–Ln_2O_3. This sequence agrees in principle with the increase in thermal stability and melting points. The rule of additivity does not then hold when sulphur is replaced by oxygen. Thus the complete oxidation of the sulphide to the oxide ($La_2S_3 + 4.5O_2 \rightarrow La_2O_3 + 3SO_2$) results in the evolution of 120 kJ per mole of S, while the oxidation of the oxide sulphide to the oxide ($La_2O_2S + O_2 \rightarrow La_2O_3 + SO_2$) is accompanied by the evolution of 100 kJ per mole of S. Analogous thermodynamic properties in the series of lanthanide oxides and oxide sulphides vary in parallel, which is illustrated, in particular, in Fig.8.

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As can be seen from the data presented, the methods of synthesis and the crystal chemistry of the oxide sulphides have been investigated fairly completely. The thermodynamics of the lanthanide, scandium, and yttrium oxide sulphides have been investigated to a lesser extent. There are no consistent values of the principal thermodynamic functions and no reliable melting points, which could be used to characterise newly obtained compounds. Bearing in mind the applied importance of the oxide sulphides, namely their generally established application in the technology of phosphors, as well as the possible new fields where they may be used in the desulphurisation of metallic melts and steels and in the removal of sulphur and its gaseous compounds (H_2S, SO_2) from furnace gases and gaseous fuel, the necessity for further investigation of the high-temperature chemistry and thermodynamics of the oxide sulphides becomes understandable.

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