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Abstract

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ON LANTHANUM SULFIDES

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One lanthanum sulfide, La S , is known (not counting the polysulfide LaS , which dissociates at 660° with formation of La S), concerning which contradictory data are available. Thus, its melting points are given from 2100–2150° (1, 3) to 2750° (2), and the appearance of the product is described either as a black glassy mass ( ) or as hexagonal plates with a strong reflection, light-yellow or orange in color (2).

By analogy with the cerium sulfides (,), it was assumed that, besides lanthanum sesquisulfide, lower sulfides also exist, in particular the monosulfide LaS, which should be more refractory than La S and may be of interest as a high-temperature refractory material. We obtained this compound and investigated some of its properties.

The starting materials were lanthanum nitrate and metallic lanthanum of the following chemical composition: La(NO) : La O in ΣR O > 99.5%, Fe traces, Si traces; La:R O = 99.8%, including La 99.7%, Fe 0.01%, Si ~0.05%.

20 g of loosely poured lanthanum nitrate powder were chlorinated in a quartz ampoule with CCl vapors passed through at a rate of about 50 cm^3/hr at 800 ± 5° for 3 hr. The CCl had previously been dehydrated with phosphorus pentoxide, followed by triple distillation.

The chlorination product—a white, non-sintered crystalline powder with particle size up to 0.5 mm—dissolved in water without residue and, according to analysis, contained 43.2% Cl (theoretical Cl content in LaCl , 43.4%), which indicated complete chlorination. Owing to the extremely high hygroscopicity of the chloride, all manipulations with it were carried out in a sealed chamber in an atmosphere of dry argon.

Lanthanum trichloride was sulfided in the same quartz ampoule at 800° in a stream of dry hydrogen sulfide. The holding time for a 20 g charge was 3 hr; the H S flow rate was 4 l/hr.

Traces of moisture in the hydrogen sulfide were frozen out in a trap cooled with solid carbon dioxide or with a mixture of gasoline and liquid nitrogen at the initial condensation temperature of H S (63–65°).

The sulfidation product—a non-sintered crystalline powder of cinnabar-red color, with grain size up to 0.5 mm—contained, according to chemical analysis, 25.4% S (26.5% theoretical), which corresponds to the formula La S . Like other rare-earth sulfides, La S undergoes hydrolysis under the action of atmospheric moisture. Therefore all subsequent operations with it were carried out in a special "dry" chamber in an argon atmosphere dried by passage through a trap with liquid nitrogen.

Calcination of pellets made from La S at 1700–1800° in a vacuum of 10 -10 mm Hg leads to a change in its original color to dark gray. (Pellets weighing ~1 g, pressed from La S powder that had been ground and sieved through a sieve with 74   openings, were placed in tantalum crucibles with lids and quickly transferred from the "dry" chamber into the furnace.)

In this case the weight loss was ~0.8%, and the shrinkage ~3.3%. On rapid cooling, cracks appeared in the specimens, which indicated the poor thermal-shock resistance of the material. Chemical analysis of the gray product showed a lower sulfur content than in the initial red La_2S_3—only 22.37%, which, by analogy with the sulfides of cerium, apparently corresponded to a solid solution La_2S_3—La_3S_4.

When heated in the same furnace at 2000° for 40 min, the tablets of La_2S_3 melted and evaporated, while a small amount of condensate formed on the lid of the crucible in the form of shiny black crystals. X-ray analysis of them gave a powder pattern with clear, sharp lines belonging to a hexagonal structure of the cerium oxysulfide type ([6]).

Thus, on heating in a high vacuum to 1800°, partial evaporation and decomposition of La_2S_3 take place. A new sulfide of composition La_2S_3—La_3S_4 is formed, melting in the range 1800–2000° and readily volatile, the vapors of which are oxidized by the residual oxygen in the vacuum to the slightly volatile and more refractory $La_2O_2S_3$.

LaS was obtained by reducing La_2S_3 with metallic lanthanum by the "impregnation" method. For this purpose, porous crucibles of 0.5 cm^3 capacity were prepared from La_2S_3 by pressing under a pressure of 1 t/cm^2 and firing in a vacuum of 10^4—10^{-5} mm Hg at a temperature of 1800° for 10 min, with slow cooling. Metallic lanthanum, previously mechanically cleaned of surface oxide films, was charged into the crucible in amounts somewhat exceeding the stoichiometric amount, and the crucible was placed in a vacuum furnace. The reaction of the liquid metal, penetrating into the pores of the crucible by capillary forces, began already at 1250°, but proceeded very slowly. Good results were obtained at 1600° and a holding time of 10 min.

The reaction product was a golden-yellow substance with a sulfur content of 19.7% (the theoretical sulfur content in LaS is 18.75%).

A powder X-ray pattern, with lines belonging to only one cubic phase, showed that this substance, isostructural with CeS, crystallizes with a NaCl-type lattice with an identity period of 5.83 ± 0.01 kX, which gives a calculated density of 5.36 g/cm. Thus, this substance was identified as lanthanum monosulfide, LaS.

The microstructure of the prepared LaS is two-phase: large oval yellow grains of LaS, along whose boundaries a light-gray phase is located (judging by weak etching in CH_3COOH), lanthanum oxysulfide. Estimation of the area occupied by the phases showed that the monosulfide had the following composition: LaS 95-97%, oxysulfide ~3-5%. The Vickers microhardness of LaS (yellow grains) under a 20 g load is 197 ± 1.5 kg/mm², which indicates its metallic character. On heating in vacuum to 2100°, it was not possible to melt pieces of LaS.

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Note: Figure translations are in progress. See original paper for figures.