Chemistry

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1964

SovietRxiv

Abstract

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SYNTHESIS OF NEW SILICATES OF RARE-EARTH ELEMENTS

The features of the structure of the electron shells of the atoms of the rare-earth elements, yttrium and scandium made it possible to predict interesting properties for a number of compounds of these elements, and in particular for silicates of rare-earth metals. This new class of silicates, possessing special crystallo-optical and other physical properties, was synthesized and studied in our laboratory ($^{1-3}$).

The first stage of this large systematic work was the investigation of phase diagrams of the binary systems Ln_2O_3—SiO_2 (^{4,5}). The investigation of the systems was combined with a detailed study of the physicochemical properties of the crystalline and glassy phases that formed. The second stage consisted of work on studying mutual solid solutions between isostructural silicates of rare-earth metals ($^{7-9}$).

The third stage was phase diagrams of systems whose components are, on the one hand, silicates of the first and second groups of the periodic system, and, on the other, silicates of rare-earth elements ($^{10-12}$). A special section was represented by work on studying liquation phenomena in two- and three-component silicate systems with rare-earth elements ($^{13-15}$).

The fifth stage is the synthesis of single crystals of rare-earth metal silicates obtained in the study of phase diagrams of the systems. These single crystals are used for structural and other investigations carried out in specialized laboratories. It should also be noted that syntheses have been performed of certain analogs of natural minerals, such as thalenite ($Y_2Si_2O_7$), yttrialite $(Y, Th)_2Si_2O_7$, as well as the preparation of glasses with interesting spectral properties. An important section is represented by investigations of rare-earth-element silicates in the divalent state (samarium, europium, ytterbium). In addition to silicates previously obtained and studied, in 1962 we synthesized europium silicates of three types: oxyortho-$Eu_2O_3 \cdot SiO_2$ ($Eu_2O[SiO_4]$), ortho-2 $Eu_2O_3 \cdot 3SiO_2$ ($Eu_4[SiO_4]_3$), and diorthosilicate-$Eu_2O_3 \cdot 2SiO_2$ ($Eu_2Si_2O_7$), which are analogs of compounds previously described by us in other systems. The compound $Eu_2O_3 \cdot SiO_2$ $(1:1)$ melts without decomposition at a temperature of $1980 \pm 30^\circ$. Its crystals have refractive indices: $n_g = 1.890$, $n_p = 1.870$,

Fig. 1. Single crystals of lanthanum oxyorthosilicate–$La_2O[SiO_4]$ (a); ytterbium diorthosilicate–$Yb_2Si_2O_7$ (b); yttrium silicate–$Y_2O[SiO_4]$ (c); europium silicate–$Eu_2O[SiO_4]$ (d). 9×

Figure 1: Fig. 1. Single crystals of lanthanum oxyorthosilicate–$La_2O[SiO_4]$ (a); ytterbium diorthosilicate–$Yb_2Si_2O_7$ (b); yttrium silicate–$Y_2O[SiO_4]$ (c); europium silicate–$Eu_2O[SiO_4]$ (d). 9×

birefringence $(n_g - n_p) = 0.020$, biaxial, optically positive, with straight extinction.

The compound $2Eu_2O_3 \cdot 3SiO_3$ (2 : 3) melts without decomposition at a temperature of 1950 ± 30°. This compound is stable in the temperature interval 1950—1650°. At 1650° it decomposes into a mixture of compounds 1 : 1 and 1 : 2. Its crystallo-optical constants are as follows: refractive indices $n_o = 1.865$, $n_e = 1.845$, birefringence $(n_o - n_e) = 0.020$, uniaxial, optically negative; it is characterized by hexagonal symmetry. The compound $Eu_2O_3 \cdot 2SiO_2$ (1 : 2) melts at a temperature of 1760 ± 30° with decomposition into $2Eu_2O_3 \cdot 3SiO_2$ and liquid. Microscopic investigations showed that the crystals of this silicate are biaxial, optically positive, with refractive indices: $n_g = 1.775$, $n_p = 1.763$, birefringence $(n_g - n_p) = 0.012$.

Fig. 1. Single crystals of lanthanum oxyorthosilicate–$La_2O[SiO_4]$ (*a*); ytterbium diorthosilicate–$Yb_2Si_2O_7$ (*b*); yttrium silicate–$Y_2O[SiO_4]$ (*c*); europium silicate–$Eu_2O[SiO_4]$ (*d*). 9×

In works ([16], [17]) it was established that europium silicates occupy an intermediate position between the first and second structural subgroups characteristic of the silicates of rare-earth elements. Further experiments showed that, when isomorphic admixtures of compounds of the second subgroup (yttrium, gadolinium, or dysprosium) are introduced into the composition of these silicates, their structures become similar to the structures of the silicates of this second subgroup.

In the course of further investigation of the properties of the obtained compounds of rare-earth elements, beginning in 1962, we for the first time grew single crystals of a number of silicates of rare-earth metals. No information on this question is available in the literature. For growing single crystals of silicates we used the method of synthesis from solution in a melt of the low-melting salt potassium fluoride.

The compounds, initially obtained by the coprecipitation method in the corresponding stoichiometric ratios, were then subjected to prolonged thermal treatment (heating and slow cooling at a rate of 1.5-1° per hour) in closed platinum crucibles in furnaces with platinum-rhodium heaters. In this way homogeneous single crystals were obtained of oxyorthosilicates of lanthanum, samarium, europium, ytterbium, yttrium, and scandium, of ytterbium diorthosilicate, and of yttrium silicate with the garnet structure.

The quality of the synthesized products was monitored by crystallo-optical and X-ray phase analysis, as well as by infrared spectroscopy. The composition of the obtained crystals was determined by chemical analysis. Figure 1*a* shows a photograph of single crystals of oxyorthosi-

lanthanum silicate $La_2O[SiO_4]$. These crystals have an elongated form and a columnar habit. Plate-like crystals of ytterbium diorthosilicate are shown in Fig. 16. A comparison of the crystal-optical characteristics of polycrystalline and single-crystal specimens shows their structural and chemical identity. Fig. 16 illustrates single crystals of yttrium oxyorthosilicate $Y_2O[SiO_4]$, with clearly expressed faces. Fig. 12 gives a photograph of crystals of europium oxyorthosilicate. At present, the fine structure and other properties of the products obtained are being studied.

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Received
21 IV 1964

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