RARE-EARTH SILICATES

COMMUNICATION 1. PHASE DIAGRAM OF THE SYSTEM La₂O₃-SiO₂

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The study of the properties of rare-earth elements, their reactions with each other and with other elements, and their use in various fields of the national economy has been developed particularly in recent years both abroad and in the Soviet Union [1-4]. In the foreign literature, many papers have been devoted to the chemistry, metallurgy, and problems in the separation and application of rare-earth elements, and promising developments in this scientific field have been presented. Thus, the U. S. Bureau of Mines planned a large program of fundamental research on the refractory properties of rare-earth oxides individually and in combination with other oxides [5]. The study of phase diagrams of systems containing rare-earth oxides is a new section of the physical chemistry of silicates.

As follows from a review of the literature, the reaction of silica with rare-earth oxides has hardly been studied. In the Institute of Silicate Chemistry, a large program of work has been planned for the study of phase diagrams of systems containing silica and oxides of rare and disperse elements, and the investigation of the physical and physicochemical properties of crystalline and vitreous phases of these systems. The purpose of the present work was a study of phase diagram of the binary system La₂O₃-SiO₂.

EXPERIMENTAL

The following materials were used for the preparation of samples: silica in the form of a fine powder (99.90% SiO₂) and lanthanum oxide, containing up to 0.7% of impurities (Nd₂O₃, CeO₂, PrO₂, Ca, Fe). Homogeneous samples were obtained, and specimens quenched and annealed by the procedure we described previously [6]. The samples were investigated under a microscope and by x-ray structural analysis. The refractive indices of highly refractive substances were determined on a modernized MIS-11 microscope.

Since there is a possibility of a change in the valence of lanthanum at high temperatures in a stream of argon, the degree of reduction of La₂O₃ to LaO was checked by two methods: 1) by firing a sample which had been fired in a microfurnace in a mullite furnace and determining the increase in weight (LaO is converted to La₂O₃); 2) by a volumetric method (oxidation of LaO to La₂O₃ with permanganate solution and titration with oxalic acid). As the experiments showed, the LaO content of a sample from pure lanthanum oxide after heating was small and increased with a rise in temperature:

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>LaO Content (weight %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1800</td>
<td>0.15</td>
</tr>
<tr>
<td>1900</td>
<td>0.30</td>
</tr>
<tr>
<td>2000</td>
<td>0.50</td>
</tr>
<tr>
<td>2100</td>
<td>0.65</td>
</tr>
</tbody>
</table>
RESULTS OF INVESTIGATION

The general form of the phase diagram we obtained for the system La$_2$O$_3$-SiO$_2$ is given in Figs. 1a and b. As Fig. 1 shows, a chemical compound with the composition 2La$_2$O$_3$·3SiO$_2$ (78.3 weight % of La$_2$O$_3$ and 21.7 weight % of SiO$_2$) is formed in the system and layer formation occurs.

There are two eutectics on the phase diagram of the system: One is formed between lanthanum oxide and the compound 2La$_2$O$_3$·3SiO$_2$ at 1700°C and the composition 87.5 weight % (56.3 mol. %) of La$_2$O$_3$ and 12.5 weight % (43.7 mol. %) of SiO$_2$; the second is formed between the compound 2La$_2$O$_3$·3SiO$_2$ and cristobalite at 1600°C and a composition of 65 weight % (24.7 mol. %) of La$_2$O$_3$ and 35 weight % (75.3 mol. %) of SiO$_2$.

The compound 2La$_2$O$_3$·3SiO$_2$. The compound 2La$_2$O$_3$·3SiO$_2$, found in the system, melted without decomposition at 2020±50°C. The rapid crystallization of this silicate from the melt made it impossible to quench a melt of this composition in the form of a glass. The compound 2La$_2$O$_3$·3SiO$_2$ belongs to the hexagonal crystal system. Photomicrographs of its crystals are shown in Fig. 2a and b. Lanthanum silicate separates in the form of hexagonal platelets with white and orange interference colors in polarized light in thin polished sections. The mean refractive index of crystals of this compound equaled 1.854±0.05. The microhardness, determined on a PMT-3 apparatus, was 655 kg/mm$^2$, which corresponds approximately to the hardness of apatite (536 kg/mm$^2$) and albite (795 kg/mm$^2$). These correspond to the values 5 (apatite) and 6 (albite) on the Mohs scale.

Figure 3 shows the x-ray diffraction pattern of 2La$_2$O$_3$·3SiO$_2$, obtained with an ionization recorder, and the table gives calculated data for this diffraction pattern. The parameters of the elementary cell of 2La$_2$O$_3$·3SiO$_2$ (La$_2$Si$_2$O$_7$) have the following values: $a=11.23$ Å, $c=4.874$ Å, $c/a=0.42$. The density determined in kerosene with a pycnometer equaled 5.31 g/cc.

As calculations showed, the elementary cell contained 2 molecules and its density obtained from x-ray data equaled 5.303 g/cc. Apparently, La$_4$Si$_3$O$_{12}$ has a structure belonging to the olivine group with isolated tetrahedral [SiO$_4$]$^{4-}$ anions and lanthanum orthosilicate, La$_2$(SiO$_4$)$_3$. The chemical stability of La$_4$(SiO$_4$)$_3$, determined qualitatively with respect to hydrochloric acid, is very low. As literature data shows, low chemical stability is characteristic of the olivine group.

In Fig. 1a and b, the layer-formation region is isolated by a binodal curve. The two immiscible liquids (two glasses) are in equilibrium with cristobalite at 1650°C over the concentration range of 50-90 weight % (84.5-97.9 mol. %) of SiO$_2$. In this case the equilibrium is monotectic and is determined by the equation $L_2 = L_1 + S$ (cristobalite). The critical point of layer formation lies at 1980°C and a composition of 25 weight % (5.8 mol. %) of La$_2$O$_3$ and 75 weight % (94.2 mol. %) of SiO$_2$.

*It has now been established that two other compounds are formed in the system: La$_2$O$_3$·SiO$_2$ with refractive indices $n_D=1.875$, $n_p=1.855$; La$_2$O$_3$·2SiO$_2$ with refractive indices $n_D=1.762$, $n_p=1.752$. 

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