CHEMISTRY

Corresponding Member of the Academy of Sciences of the USSR N. A. TOROPOV, I. A. BONDAR,

1964

SovietRxiv

Abstract

Full Text

CHEMISTRY

Corresponding Member of the Academy of Sciences of the USSR N. A. TOROPOV, I. A. BONDAR,
M. M. PIRYUTKO

A NEW CRYSTALLINE MODIFICATION OF YTTRIUM ORTHOSILICATE WITH A GARNET STRUCTURE

In studying the phase diagram of the binary system yttrium oxide—silica, we for the first time obtained a polycrystalline product—yttrium orthosilicate of composition $2Y_2O_3 \cdot 3SiO_2$, or $Y_4Si_3O_{12}$ (^{1}). Crystal-optical observations made it possible to assign these crystals to the hexagonal system, with refractive indices: $n_o = 1.780$, $n_c = 1.765$.

In studying crystallization processes, the stability region of this silicate was established. It melts without decomposition at a temperature of $1950 \pm 30°$ and is stable up to 1650°. At 1650° its decomposition in the solid phase into a mixture of yttrium oxyortho- and diorthosilicate is observed. Such a decomposition phenomenon was also noted by us for a number of rare-earth orthosilicates (^{2}).

Subsequently, we grew single crystals of a number of silicates of the rare-earth elements, yttrium, and scandium from melts of low-melting salts. Yttrium silicate crystals were grown from a potassium fluoride solution by the method described by us in the Proceedings of the 3rd Conference on Crystal Growth. The crystals obtained are shown in Fig. 1. They have the form of regular isometric polyhedra with well-developed shiny faces; their dimensions made it possible to carry out goniometric measurements, performed at the Department of Crystallography of Leningrad State University named after Zhdanov. These measurements showed that the yttrium silicate single crystals belong to the cubic system; in their external bounding two simple forms are revealed: the rhombododecahedron {110} and the tetragontrioctahedron {112}. The {112} faces are more developed than the {110} faces.

Chemical analysis of this single-crystalline product showed that its composition corresponds to the formula $2Y_2O_3 \cdot 3SiO_2$ (SiO_2—28.70%, Y_2O_3—70.50%; F—0.35%; K—0.51 wt.%).

Crystal-optical analysis revealed the isotropic character of the crystals of this compound, which corresponds to their general garnet-like external appearance. The refractive index ($n = 1.82$) is higher than that of the previously obtained polycrystalline form of the same substance. The hardness is high: of the same

Fig. 1

Figure 1: Fig. 1

order as the hardness of topaz (8 on the Mohs scale). The microhardness is equal to 1300 kg/mm^2. Studies using a high-temperature microscope showed that the new garnet-like cubic form $2Y_2O_3 \cdot 3SiO_2$, upon heating, transforms into an anisotropic modification at 1550°. The reverse transition of the hexagonal form into the cubic form could not be accomplished, which indicates the monotropic character of the transformation.

The X-ray diffraction pattern of the single crystals (Fig. 2) confirmed, on the one hand, a substantial difference between the structure of this form of yttrium orthosilicate and the polycrystalline hexagonal modification, and, on the other, indicated its similarity to the structures of other synthetic and natural compounds of the garnet type.

Natural minerals of the garnet family are characterized by the general chemical formula of the type $A_3^{2+}B_2^{3+}[SiO_4]_3$ and, structurally, by the presence of isolated tetrahedra $[SiO_4]^{4-}$. In the garnet structure, individual ions have coordination numbers 8 (A), 6 (B), and 4 (Si). Representatives of nat-

natural garnets are pyralspites (pyrope $Mg_3Al_2Si_3O_{12}$, almandine $Fe_3Al_2Si_3O_{12}$, spessartine $Mn_3Al_2Si_3O_{12}$), ugrandites (uvarovite $Ca_3Cr_2Si_3O_{12}$, grossular $Ca_3Al_2Si_3O_{12}$, andradite $Ca_3Fe_2Si_3O_{12}$). In addition, hydrogarnets $3(Ca,Sr)O(Al,Fe)O_3 \cdot 3(Si,H_4)O_2$ with a peculiar isomorphous replacement of silicon by hydrogen (hydroxyls) also belong to this same family. A more general crystal-chemical consideration of various natural and synthetic substances with the garnet structure shows extraordinarily broad possibilities for isomorphous substitutions. Thus, for example, the hexahydrate of tricalcium aluminate $3CaO \cdot Al_2O_3 \cdot 6H_2O$ may be regarded as grossular in which all silicon atoms have been replaced by hydrogens $3Si \rightarrow 12H$.

Fig. 1. Single crystals of yttrium silicate $Y_4Si_3O_{12}$ (9×)

Atoms of rarer elements also participate in isomorphous substitutions. Their general crystal-chemical formula is as follows: $A_3B_2C_3O_{12}$ or $A_3B_5O_{12}$. In work (3), compounds of the garnet type $Ln_6Fe_{10}O_{24}$ were obtained, where Ln is an element of the lanthanoid group. In an earlier work (4), the existence of isomorphism between spessartine $Mn_3Al_2Si_3O_{12}$ and $Y_3Al_2O_{12}$ was shown. Here the groups MnSi are mutually replaced by YAl. The replacement of Si^{4+} by Ge^{4+} or Fe^{3+} is also known.

According to our experimental data, the new form of $Y_4Si_3O_{12}$ apparently should be isostructural with the series of aluminates of rare-earth elements and yttrium obtained by us earlier (5). This is confirmed by comparison of the X-ray patterns of the compounds $Y_4Si_3O_{12}$ (a), $Y_3Al_5O_{12}$ (b), and $Tb_3Al_5O_{12}$ (c) (Fig. 2). This figure gives the values of the interplanar spacings of the most in-

Fig. 2

Figure 2: Fig. 2

tense lines. Isostructurality is also suggested with natural garnet, in particular grossular. For one variety of such garnet (the Kedabek deposit)*, the values of the interplanar spacings—

Fig. 2. X-ray diffraction patterns of the compounds $Y_4Si_3O_{12}$–($2Y_2O_3 \cdot 3SiO_2$) (a); $Y_3Al_5O_{12}$–($3Y_2O_3 \cdot 5Al_2O_3$) (b); $Tb_3Al_5O_{12}$–($3Tb_2O_3 \cdot 5Al_2O_3$) (c)

* Its composition: SiO_2 39.12%; Al_2O_3 22.7%; CaO 35.85%; loss on ignition—0.16 wt.%.

···the corresponding spacings and intensities are: 2.99–10; 2.66–10; 2.42–6; 2.16–6; 1.915–8; 1.707–7; 1.639–9; 1.581–10; 1.291–9; 1.101–10, and are close to those shown in Fig. 2. If one considers in greater detail the possibilities of substitution in the yttrium-silicate and lanthanoid-aluminum structures obtained by us, on the one hand, and in natural garnets of the grossular type, on the other, then, in describing the unit cell of grossular, 96 oxygen ions should be included in its composition. Each ion is simultaneously bonded to one Si ion, one Al ion, and two Ca ions. At the same time, the [SiO_4] groups are combined in the structure with the [AlO_6] and [CaO_8] groups, which have the form of distorted Thomson cubes. The crystal-chemical formulas of the compounds take the form:

$$\mathrm{Ca}_{24}^{\mathrm{VIII}}\mathrm{Al}_{16}^{\mathrm{VI}}\mathrm{Si}_{24}^{\mathrm{IV}}\mathrm{O}_{96}, \quad \mathrm{Ln}_{24}^{\mathrm{VIII}}\mathrm{Al}_{16}^{\mathrm{VI}}\mathrm{Al}_{24}^{\mathrm{IV}}\mathrm{O}_{96}, \quad \mathrm{Y}_{16}^{\mathrm{VIII}}\mathrm{Y}_{16}^{\mathrm{VI}}\mathrm{Si}_{24}^{\mathrm{IV}}\mathrm{O}_{96}.$$

As is evident from the formulas, 56 atoms of yttrium-silicate garnet (32 + 24 Si) must replace in the structure 64 atoms of aluminum garnet (24 Ln + 40 Al) or 64 atoms of grossular (24 Ca + 16 Al + 24 Si). Thus, heterovalent substitution will occur here within the limits of preservation of the electroneutrality of the lattice. The question of the possibility either of the formation of vacancies upon substitution in the unit cell of 64 Ca, Al, and Si ions or Ln and Al ions by 56 Y and Si ions, or of substitution accompanied by a change in the coordination number of oxygen, can be resolved only by direct X-ray structural methods.

Institute of Silicate Chemistry
Academy of Sciences of the USSR

Received
20 I 1964

REFERENCES

1. N. A. Toropov, I. A. Bondar’ , *Izv. AN SSSR, OKhN*, 1961, No. 4, 544.

2. I. A. Bondar' , L. N. Koroleva, N. A. Toropov, *Proceedings of the Fifth Conference on Experimental and Technical Mineralogy and Petrography*, Publishing House of the Academy of Sciences of the USSR, 1961, p. 303.

3. M. L. Keith, R. Roy, *Am. Mineral.*, **39**, 1 (1954).

4. H. S. Yoder, M. L. Keith, *Am. Mineral.*, **36**, 519 (1951).

5. I. A. Bondar' , *Proceedings of the VII Conference on the Silicate Industry*, Budapest, 1963.

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.