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Abstract

Full Text

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A NEW RARE-EARTH DIORTHOSILICATE, $K_3Eu(Si_2O_7)$

As reported earlier ([1], [2]), we have synthesized and investigated a series of single crystals of silicates of rare-earth elements: oxyorthosilicates of lanthanum, samarium, neodymium, europium, and ytterbium ($Ln_2O[SiO_4]$), diorthosilicates of europium and ytterbium ($Ln_2Si_2O_7$), yttrium silicate with the garnet structure $Y_4Si_3O_{12}$, and others.

In the present communication, single crystals of europium and potassium diortho-(pyro)-silicate—$K_3Eu(Si_2O_7)$—are described. The synthesis of this silicate was carried out from a solution in a KF melt in a platinum-rhodium furnace with programmed slow cooling (the average cooling rate was ~ 1°/hour). The duration of the experiment was 16 days. As a result, single crystals were obtained that made it possible to carry out microscopic, goniometric, spectroscopic, and X-ray investigations.

Fig. 1. Crystals of europium and potassium silicate
$K_3Eu(Si_2O_7)$

Fig. 2. General appearance of the crystals

The crystals are shown in Fig. 1. They have the form of equiaxial plates with refractive indices $n_o = 1.713$; $n_e = 1.709$, weak birefringence (0.004); the crystals are optically positive, uniaxial. The density, determined pycnometrically in kerosene, is $d^{25} = 3.41$ g/cm^3. Goniometric measurements showed that the crystals belong to the hexagonal system, of the dihexagonal-dipyramidal symmetry type ($6/mmm$). In their external faceting the silicate crystals have well-developed faces of the dihexagonal prism $(11\bar{2}0)$, the hexagonal pyramid

Fig. 3. IR absorption spectrum of K3Eu(Si2O7). (IKS-14 spectrometer, sample—a pellet in KBr, weight 2 g, diameter 25 mm, substance content 5 mg)

Figure 3: Fig. 3. IR absorption spectrum of K3Eu(Si2O7). (IKS-14 spectrometer, sample—a pellet in KBr, weight 2 g, diameter 25 mm, substance content 5 mg)

$(10\bar{1}1)$, and the pinacoid (0001). The general appearance of such a crystal is shown in Fig. 2.

The infrared spectrum, shown in Fig. 3, reveals, along with groups of bands in the ranges 1000-850 and 550-400 cm^{-1}, a single

a band of medium intensity at 685 cm^{-1}. This band may be assigned to the symmetric stretching vibration of the Si—O—Si bond (ν_s SiOSi) and, consequently, indicates the presence of condensed silico-oxygen tetrahedra in the structure. At the same time, the existence of only one band in the frequency region of ν_s SiOSi makes it possible to assume the presence of diortho-groups Si_2O_7 (^{3}, ^{4}), which agrees well with the Si:O content ratio, very close to $1 : 3.5$, according to chemical analysis.

Fig. 3. IR absorption spectrum of $K_3Eu(Si_2O_7)$. (IKS-14 spectrometer, sample —a pellet in KBr, weight 2 g, diameter 25 mm, substance content 5 mg)

It should also be noted that the activity of the ν_s SiOSi vibration in the IR spectrum indicates non-centrosymmetry of the Si_2O_7 ions ($\angle \text{SiOSi} < 180^\circ$).

Table 1 gives the assignment of frequencies for the symmetry of the Si_2O_7 ion $C_{2v} = mm$.

From rotation radiographs and Weissenberg photographs it was established that the crystal belongs to the hexagonal system—Laue class $6/mmm$. The unit-cell parameters are $a = 9.98 \pm 0.01$ Å, $c = 14.44 \pm 0.02$ Å. Comparison of these data with the spectroscopically established presence of Si_2O_7 ions makes it possible to propose the formula of the compound obtained as $3K_2O \cdot Eu_2O_3 \cdot 4SiO_2 = 2[K_3Eu(Si_2O_7)]$. This formula agrees satisfactorily with the chemical-analysis data:

Found (products of two different syntheses), %: K_2O 28.91, 28.68; Eu_2O_3 43.24, 43.61; SiO_2 26.61, 26.52

$K_3Eu(Si_2O_7)$. Calculated, %: K_2O 32.30; Eu_2O_3 40.24; SiO_2 27.46

Some difference between the calculated and found oxide contents can be explained by the possibility of replacement of potassium positions by europium in the diorthosilicate.

With 6 formula units of $K_3Eu(Si_2O_7)$ entering the unit cell, the calculated density is 3.50 g/cm^3, which is in good agreement with the experimental value. The presence in X-ray goniometric surveys of systematic extinctions $hh0l$ for all $l = 2n + 1$ leads to three possible space groups: $C_{6v}^3 = P6_3cm$, $D_{3h}^2 = P\bar{6}C2$, $D_{6h}^3 = P6_3/mcm$; however, the symmetry of the external form of the crystal argues in favor of the last. Since the possible local symmetry of the noncentrosymmetric Si_2O_7 ions (i.e., the symmetry of the special positions of the "bridging" O atoms) is limited to the groups mm, m, and 2, the placement of six of these ions in a crystal with symmetry $P6_3/mcm$ is unambiguously determined by a sixfold set of special positions with symmetry mm. It follows from the above that the crystal under investigation is potassium europium diorthosilicate, $K_3Eu(Si_2O_7)$; therefore, the analogy between this compound and the recently described pyrosilicates and pyrogermanates of the type $X_2Pb(Z_2O_7)$, where $X = K, Rb, Cs$; $Z = Si, Ge$ (5), is of some interest. The structure of $K_2Pb_2(Si_2O_7)$, studied

Table 1

Frequencies of absorption maxima in the IR spectrum of $K_3Eu(Si_2O_7)$

Frequency (cm^{-1}) and intensity	Assignment
1100 very weak	
985 shoulder	ν_{as} SiO_3 $(B_2,\ A_1)$
968 very strong	ν'_{as} SiO_3 $(B_1,\ A_2)$
938 very strong	ν_s SiO_3 (A_1)
920 shoulder	ν'_s SiO_3 (B_1)
870 very strong	ν_{as} SiOSi (B_1)
685 medium	ν_s SiOSi (A_1)
531 shoulder	δ Si_2O_7
521 medium	and
497 strong	ν Eu—O
446 strong	

Note. v. s. —very strong, s. —strong, med. —medium, w. —weak, sh. —shoulder, v. w. —very weak shoulder, sh. – "shoulder" on the slope of a stronger band.

Narai-Szabó (^{6}), is characterized by layers of composition $Pb_2Si_2O_7$ with centrosymmetric Si_2O_7 groups, which are linked to one another by Pb atoms in trigonal coordination with respect to oxygen. The layers are separated by large potassium cations (coordination number = 9). There are grounds for assuming the existence of layers of composition $EuSi_2O_7$ in the crystal $K_3Eu(Si_2O_7)$, but the Si_2O_7 groups are noncentrosymmetric. From the standpoint of the considerations expressed earlier concerning the dependence of the magnitude of the SiOSi angle in Si_2O_7 ions on the degree of covalency of the bonds of the "terminal" oxygen atoms with cations (^{4}, ^{7}), the decrease in SiOSi on going from $K_2Pb_2(Si_2O_7)$ to $K_3Eu(Si_2O_7)$ can be explained by a decrease in the covalency of the Eu–O bonds in comparison with Pb–O and by an increase in the relative content of K^+ ions.

A complete determination of the structure of $K_3Eu(Si_2O_7)$ will be carried out later.

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