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Abstract

Full Text

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FERROELECTRIC PROPERTIES OF THE MINERAL STIBIOTANTALITE

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We have discovered ferroelectric and high electro-optical properties in natural stibiotantalite $Sb(Ta, Nb)O_4$ in the temperature region below 400°C.

Natural stibiotantalite occurs in the form of polysynthetic twins having a cleavage plane perpendicular to a second-order axis (^{1,2}). X-ray studies of minerals from deposits in Australia and California (^{2}) determined the space group $Pna2_1$, the unit-cell parameters $a = 4.916$ Å, $b = 5.542$ Å, $c = 11.78$ Å (Fig. 1), and the atomic coordinates. Studies (^{6,7}) of pure synthesized compounds $SbTaO_4$ and $SbNbO_4$ confirmed these data.

Reports on the physical properties of natural stibiotantalite crystals are devoted mainly to measurements of the dispersion of refractive indices and of the angle of the optical axes, their relation to the density of the specimens (^{1}), and to the qualitative detection of piezo- and pyroelectricity (^{1,3,10}). In particular, it was indicated that the relative content of Ta and Nb in the specimens strongly affects their physical properties (density, color, refractive coefficients, etc.).

Fig. 1. Structure of the mineral stibiotantalite $SbTaO_4$

Method and results of the investigations

We had at our disposal three specimens of natural stibiotantalite from the Alto Rigondo deposit (Mozambique). All specimens were cleaved along the cleavage plane. Orientation of the specimens from X-ray patterns confirmed that the cleavage plane is perpendicular to the second-order axis.

The specific gravity of the specimens, measured by weighing in a liquid of known density, was 7.28 ± 0.17 g/cm^3. In one of the specimens (specific gravity

Fig. 2 and Fig. 3

Figure 2: Fig. 2 and Fig. 3

7.14 g/cm^3), X-ray spectral analysis determined the percentage content of tantalum, niobium, bismuth, iron, and zinc. Tantalum was determined from the L_α-line, niobium from the K_α-line of a LiF crystal in first-order reflection. The specimen contained 34.6% tantalum, 3.38% niobium, 0.5% iron and zinc, and 7% bismuth. Such a considerable amount of bismuth is characteristic of natural specimens ([1,2]).

To study the electrical properties of the specimens, silver electrodes were fired onto their polar sections. The temperature dependences of the dielectric permittivity $\varepsilon(T)$, spontaneous polarization $P_s(T)$,

the coercive field $E_k(T)$, and the pyroelectric coefficient were measured under conditions of automatic stabilization of the sample temperature with an accuracy no worse than 0.02°. The dielectric permittivity was determined in a field of less than 1 V/cm at a frequency of 1 kHz. The values of the spontaneous polarization and the coercive field were calculated from dielectric hysteresis loops at a frequency of 1 kHz and an applied-field amplitude of 5.4 kV/cm. The pyroelectric coefficient was measured by the static compensation method ([11]).

Fig. 2. Temperature dependences of the dielectric permittivity $\varepsilon(T)$, spontaneous polarization $P_s(T)$, and coercive field $E_k(T)$ for the mineral stibiotantalite

Fig. 3. Dependence of the dielectric permittivity ε on temperature for the second and third samples of stibiotantalite, with thicknesses of 3.2 mm *(1)* and 1 mm *(2)*

In Fig. 2 are shown the dependences $\varepsilon(T)$, $P_s(T)$, and $E_k(T)$ for the first sample. The value of the pyroelectric coefficient of this sample was 50 CGSE units and was constant in the interval $40 \div 100°$. Extrapolation of the value P_s, measured at 250°, to room temperature with allowance for the pyroelectric coefficient gives a spontaneous polarization at 20° equal to 16.8 μC/cm^2 ($5 \cdot 10^4$ CGSE units). The value of E_k at 20° is close to the breakdown value, which makes direct measurement of P_s at room temperature difficult.

Figure 3 shows the dependences $\varepsilon(T)$ for the second and third samples. The third sample had a thickness of 1 mm and was cleaved from the second, whose thickness was 3.2 mm. For the thin sample, simultaneously with a shift of the Curie point by 5° toward lower temperatures, an increase in the peak of the dielectric permittivity is observed, which is apparently associated with an improvement in the homogeneity of the sample composition. This was also indicated by the absence of unipolarity of the dielectric hysteresis loops and, accordingly ([12]), by a small (in the interval 40—250°, about 6 CGSE units) pyroelectric coefficient.

The value of the piezoelectric modulus of the first sample under hydrostatic compression is $3.54 \cdot 10^{-6}$ CGSE units/dyne.

Observation of the transverse electro-optic effect was carried out by the interference method. For the ratio $l/d = 1.8$ and the refractive-index value 2.4 (^{1}), the electro-optic coefficients at a wavelength of 0.63 μ are equal to

$$r_{33} \simeq 78 \cdot 10^{-8} \text{ CGSE units},$$

$$r_1 = a_1 r_{13} + a_2 r_{23} \simeq 40.5 \cdot 10^{-8} \text{ CGSE units}.$$

The half-wave voltages have values of 1 and 1.9 kV, respectively. Comparison with the values of the electro-optic coefficients of other materials: $30 \cdot 10^{-8}$ CGSE units for KH_2PO_4 (KDP) (^{14}), $90 \cdot 10^{-8}$ CGSE units for $LiNbO_3$ (^{15}), makes it possible to conclude that the use of stibiotantalite in electro-optics is promising.

Discussion of the Results

On the basis of their chemical composition, the stibiotantalite minerals studied may be assigned to the solid solution of stibiotantalite and bismutotantalite,

$$\mathrm{Sb(Ta,Nb)O_4 \cdot Bi(Ta,Nb)O_4}.$$

Natural crystals of stibiotantalite and bismutotantalite are isomorphous (^{2,4}).

In all the specimens studied, properties characteristic of ferroelectrics were observed, such as the anomalous character of the dependence $\varepsilon(T)$, dielectric hysteresis loops, and increased pyroelectric activity. The coincidence of the temperatures of the maximum of the dielectric permittivity and of the disappearance of spontaneous polarization indicates a phase transition in the region of 400°.

The temperature dependence of the reciprocal dielectric permittivity, $1/\varepsilon(T)$, obeys the Curie–Weiss law with the constant

$$C = (2.49 \pm 0.67) \cdot 10^5 \text{ deg}.$$

The "factor-of-two" law (2 ± 0.2) is satisfied with good accuracy (Fig. 4).

Analysis carried out within the framework of the Ginzburg–Devonshire theory using the data of Figs. 2 and 4, under the assumption that the phase transition in stibiotantalite is a second-order phase transition, gives, in the expansion

$$\Phi = \Phi_0 + A(T - T_0)P^2 + BP^4,$$

the following values of the coefficients:

$$A = 3.98 \cdot 10^5 \text{ deg}^{-1}, \qquad B = 2.88 \cdot 10^{-12} \text{ cm}^4 \cdot (\text{CGSE units})^{-2}.$$

Fig. 4. Plot of the dependence $1/\varepsilon(T)$ according to the data of Fig. 2

Figure 3: Fig. 4. Plot of the dependence $1/\varepsilon(T)$ according to the data of Fig. 2

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The quantitative difference in the parameters of individual specimens can be explained primarily by differences in the chemical composition of the specimens. The specific gravity of the specimens studied varies within ±2.5% (with an error in the density determination of no more than ±0.2%). Since the pure compositions $SbTaO_4$ and $SbNbO_4$ differ in density by only 14%, the observed difference indicates variations in the percentage content of Ta, Nb, and Bi in the compounds and their possible nonstoichiometry.

Stibiotantalite is a ferroelectric of the oxygen-octahedral type with the chemical formula $A^{III}B^{V}O_4$. By analogy with known compounds, it may be assumed that the phase transition in stibiotantalite belongs to displacement-type transitions. The A and B ions in the structure of stibiotantalite are located at the centers of somewhat distorted oxygen octahedra (Fig. 1).

In accordance with the Smolenskii—Matthias criterion ([12]) for the existence of spontaneous polarization in ferroelectrics of the oxygen-octahedral type, the appearance of spontaneous polarization in stibiotantalite is probably due to displacement of the B ion in the oxygen octahedron, since the A cation, after giving up its valence electrons, will not have the electronic structure of a noble gas. Larger values of spontaneous polarization should be expected from isostructural compounds containing niobium.

A series of such structures of the type $A^{III}B^{V}O_4$ includes the compounds Sb_2O_4 ($Sb^{III}Sb^{V}O_4$), $SbNbO_4$, $SbTaO_4$, $BiNbO_4$, $BiTaO_4$ ([2,4,7]), and their solid solutions. In the synthesis of the compounds $BiNbO_4$ and $BiTaO_4$ it was established that only the low-temperature phase (up to 1020°) is isostructural with stibiotantalite ([5,6,7]).

In works ([5,8,9]) the preparation of an entire series of compounds of the type $A^{III}B^{V}O_4$ was reported, where A is yttrium, lanthanides, indium, scandium, iron, and B is tantalum, niobium, vanadium, but none of the compounds obtained had the stibiotantalite structure. In ([5]) it was noted that the synthesis of $As(Ta, Nb)O_4$ is very difficult. Despite the difficulties noted, the study of compounds belonging to the named isostructural series is highly promising.

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