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OPTICAL PROPERTIES

Investigation of the Ferroelastic Phase Transition in the $SrMgF_4$ Pyroelectric Crystal

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Abstract—A $SrMgF_4$ compound has been synthesized and a high optical-quality crystal has been grown. Optical-polarization observations, X-ray diffraction analysis, and the measurement of the birefringence $\Delta n_i(t)$ in the $SrMgF_4$ crystal have been carried out in the temperature range of 90–1200 K. A second-order improper ferroelastic phase transition accompanied by birefringence anomalies and the symmetry change $P112_1$ ($Z = 12$) $\longleftrightarrow$ $Cmc2_1$ ($Z = 4$) has been discovered at $T_0 = 478 \pm 1$ K. The crystal remains pyroelectric in both phases. Considerable contributions of the fluctuations of the order parameter have been observed in the temperature ranges of $(T_0 - T) < 15$ K and $(T - T_0) < 60$ K.

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1. INTRODUCTION

Isostructural crystals of the $BaMF_4$ family (M = Mg, Mn, Fe, Co, Ni, Zn) belong to the pyroelectric symmetry class $Cmc2_1$. Their structure is formed by chains of slightly distorted MF_6 octahedra. Combination of nonlinear optical properties with a wide transparency region (125 nm–13 μm) makes these compounds unique for optical applications in the spectrum range from ultraviolet to mid-infrared [1]. In addition, these compounds are of interest for researchers owing to the presence of phase transitions of various nature [2, 3]. $AMgF_4$ (A = Sr, Eu, Sm) crystals are less studied and, according to [4], belong to the orthorhombic symmetry class at room temperature. Testing of the optical second harmonic gave negative result; therefore the symmetry group $Cmcm$ with the parameters a = 3.917 Å, b = 14.459 Å, c = 5.637 Å, $Z = 4$ of the unit cell was chosen [4]. Later X-ray investigation of a $SrMgF_4$ crystal identified its symmetry at room temperature as monoclinic $P112_1$ with the doubled parameters a and the tripled length c with respect to the size of the unit cell of the group $Cmcm$: a = 7.825 Å, b = 7.493 Å, c = 16.925 Å, $\gamma = 105.04°$, $Z = 12$ [5].

The possibility of a structural phase transition in a $SrMgF_4$ crystal was discussed in [5–7]. The presence of local symmetry planes in the superstructure of Sr atoms at room temperature allowed Ishizawa et al. [5] to suggest the existence of a higher-symmetry high-temperature phase. In [6], the hypothesis of a phase transition arose from the observation of a thermal anomaly near $T \approx 1082$ K by the differential thermal analysis method, whereas the melting temperature of the crystal is $T_{melt} = 1153$ K. Abrahams [7] showed that the X-ray data reported in [5] satisfy the structural criteria of the existence of ferroelectricity in the crystal of interest. Moreover, he predicted the magnitude of spontaneous polarization at room temperature ($P_s \approx 11 \times 10^{-2}$ C m^{-2}, which is typical for two-dimensional ferroelectric crystals) and a phase transition to a paraelectric state at $T_c \approx 450$ K accompanied by the symmetry change $P2_1$ ($Z = 12$) $\longleftrightarrow$ $P2_1/m$ ($Z = 12$). Thus, according to rather scarce literature data, the $SrMgF_4$ crystal can be regarded as a possible polar compound suitable for various applications. However, experimental evidence for ferroelectric properties or a phase transition to the paraelectric phase in this crystal is lacking in the literature.

The present work is aimed at finding the temperature range of stability of the $SrMgF_4$ crystal structure. To reveal possible phase transitions, we studied the behavior of the crystal-optical characteristics, including birefringence, orientation of the indicatrix, and twinning in a wide temperature range, and performed X-ray experiments at two temperatures. The optical measurements were carried out in the temperature range of 90–1200 K with the use of an Axioskop-40 polarization microscope and Linkam LTS 350 and TS 1500 heating stages. Birefringence was measured to an accuracy of ±0.00001 by the Berek compensator method with the use of a Leica instrument. The structure investigation was performed on a Bruker APEX DUO automatic X-ray diffractometer (MoK_α radia-

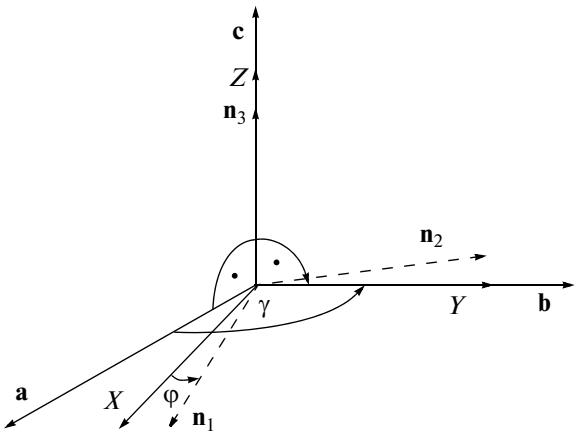

Fig. 1. Relative position of the crystallographic (**a**, **b**, **c**), physical (*X*, *Y*, *Z*), and optical ($\mathbf{n}_1$, $\mathbf{n}_2$, $\mathbf{n}_3$) coordinate systems in the $SrMgF_4$ crystal at room temperature. The angles are $\gamma = 105.04°$ and $\varphi \approx 0.6°$.

tion, a graphite monochromator, and a CCD detector) in the angle range $\theta = 2.41°–28.28°$ at the temperatures $T_1 = 300$ K and $T_2 = 623$ K.

2. CRYSTAL GROWTH

$SrMgF_4$ was synthesized from a mixture of fluorides SrF_2 and MgF_2 at a temperature of 1670 K in the presence of fluorant (CF_4). To remove oxygen-containing impurities the initial components were precalcined for 24 h in dynamic vacuum at a temperature of 770 K. A tapered glass-graphite crucible was filled with the synthesized material and placed in a hermetically sealed quartz tube evacuated to a pressure of 10^{-1} Pa. Crystals were grown by the Bridgeman method in a two-zone furnace with temperatures of 1470 and 970 K in different zones. The velocity of the tube pulling-down was 1 mm/day and the temperature gradient in the growth region was 10–20 K/cm. Cooling was performed in the regime of the switched-off furnace. The grown transparent crystals with a volume of about 1 cm^3 were annealed in vacuum for one day.

3. EXPERIMENTAL RESULTS

The oriented (001), (010), and face-normal (*X*) cuts (Fig. 1) were used for optical investigations. This particular orientation of crystallographic, physical and optical axes (Fig. 1) in $SrMgF_4$ was chosen because, in contrast to the (100) plane, the (010) plane in this crystal exhibits good cleavage and strong X-ray reflections required for positioning the samples.

Observation through the polarization microscope showed that the view field of the (001) cut at room temperature contains a very fine barely resolved systematic streak twinning pattern (Fig. 2), the components of which differ in the extinction position by the small angle $2\varphi \approx 1°–1.5°$. The quality of the pattern depended considerably on the mechanical state of the sample. A regular pattern was formed after long-term annealing at a temperature of ~600 K. The small disorientation angle 2φ decreased during heating and the twins were resoled only up to a temperature of ≈450 K. Above this temperature, extinction of the plate became even. For two other cuts, extinction remained clear, without twins in the entire temperature range of measurements.

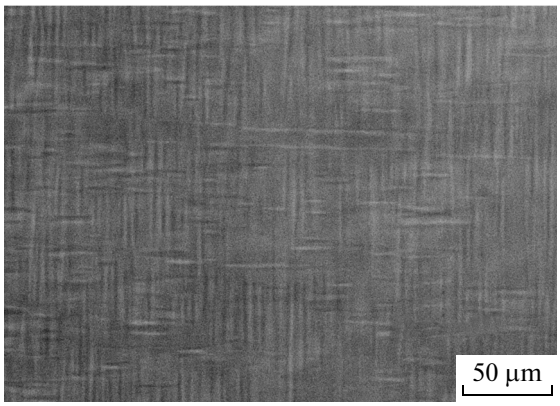

Fig. 2. Twinning structure of $SrMgF_4$ observed in the (001) cut at room temperature.

The experimental results on the temperature dependence of the birefringences $\Delta n_1(T)$, $\Delta n_2(T)$, and $\Delta n_3(T)$ in the $SrMgF_4$ crystal are shown in Fig. 3. The room-temperature values of birefringences are different: $\Delta n_1 = (n_2 - n_3) = 0.0135$, $\Delta n_2 = (n_1 - n_3) = 0.0030$

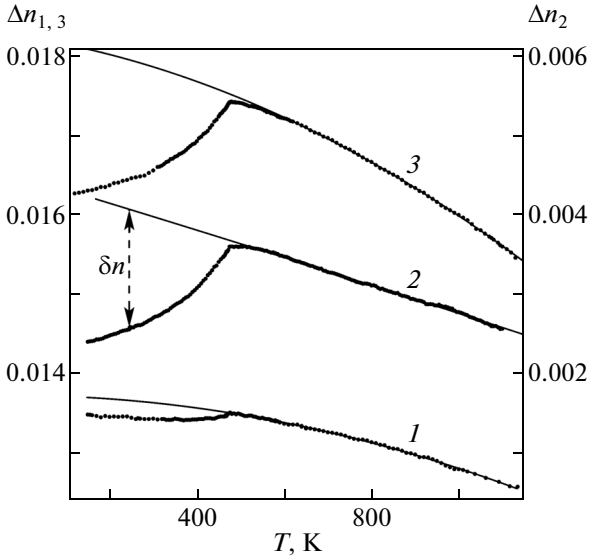

Fig. 3. Temperature dependences of the birefringence of the $SrMgF_4$ crystal: (*1*) $\Delta n_1(T)$, (*2*) $\Delta n_2(T)$, and (*3*) $\Delta n_3(T)$. δn is the anomalous part of the birefringence.

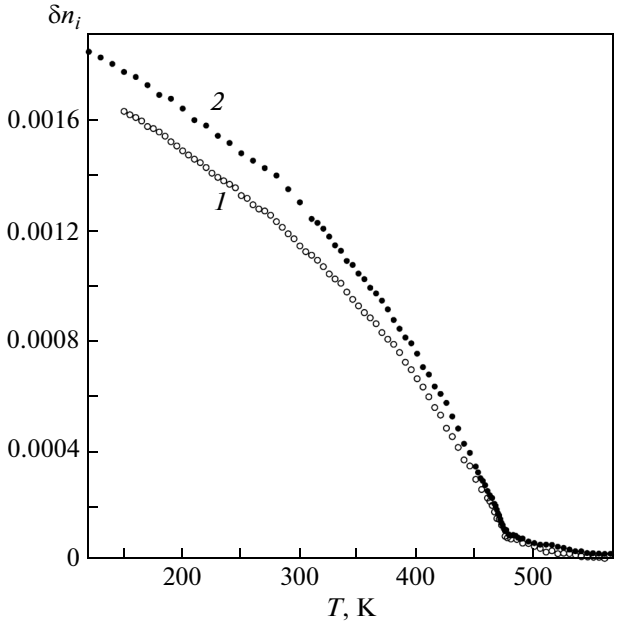

Fig. 4. Temperature dependences of the anomalous part of the birefringence of the $SrMgF_4$ crystal: (*1*) $\delta n_2(T)$ and (*2*) $\delta n_3(T)$.

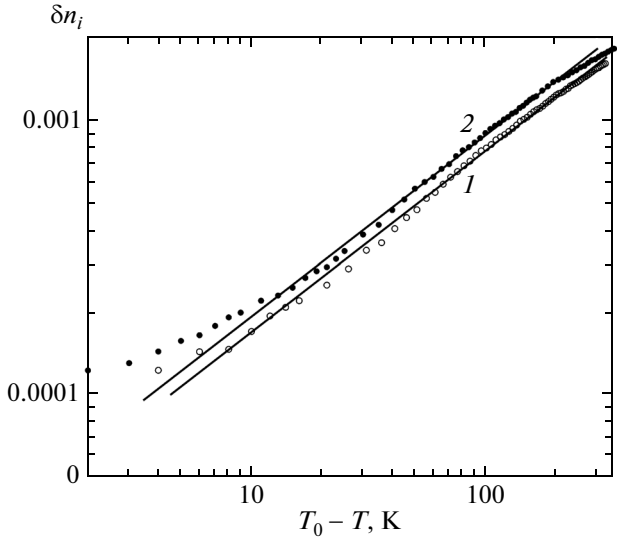

Fig. 5. Temperature dependences (*1*) $\delta n_2(T_0 - T)$ and (*2*) $\delta n_3(T_0 - T)$ for the $SrMgF_4$ crystal on the log–log scale.

and $\Delta n_3 = (n_1 - n_2) = 0.0165$. These optical characteristics exhibit anomalous behavior with a change in temperature. The dependences $\Delta n_1(T)$, $\Delta n_2(T)$, and $\Delta n_3(T)$ in a wide temperature range of 500—1130 K are smooth curves described by second-order polynomials. The character of the dependences $\Delta n_i(T)$ changes near $T \approx 480$ K and all three curves in Fig. 3 exhibit pronounced anomalies.

X-ray measurements were performed on a $0.19 \times 0.13 \times 0.11$ mm optically transparent single crystal. To obtain high temperatures, the sample was heated by a jet of hot air. At the temperature $T_1 = 300$ K, the $SrMgF_4$ crystal has monoclinic system and space group $P112_1$ with the unit-cell parameters $a = 7.8010$ Å, $b = 7.4736$ Å, $c = 16.8835$ Å, $\gamma = 105.0302°$, and $Z = 12$. These results agree well with the earlier structural data [5]. At the temperature $T_2 = 623$ K, the X-ray diffraction pattern differs significantly from the one described above. The group of reflections indicating multiplication of some lattice parameters disappears. The set of X-ray reflections of $SrMgF_4$ measured above the phase transition temperature is described by the orthorhombic symmetry $Cmc2_1$ with the lattice parameters $a_0 = 3.9369$ Å, $b_0 = 14.4884$ Å, $c_0 = 5.6379$ Å, and $Z = 4$.

4. DISCUSSION

Twinning geometry and the mutual orientation of the optical indicatrices in the neighboring twins in the $SrMgF_4$ crystal are indications of the monoclinic room-temperature phase with the twofold axis along [001], which agrees with the symmetry group $P112_1$ [5] and with our X-ray measurements described above. The angle 2φ between the optical indicatrices vanishes at the temperatures $T > 480$ K indicating that the crystal acquires a higher, orthorhombic symmetry. The X-ray experiments performed at the temperature $T_2 = 623$ K also confirmed this assumption; moreover, they allowed us to chose the polar symmetry group $Cmc2_1$ for the initial orthorhombic phase. Thus, the crystal undergoes a structural phase transition near $T = 480$ K accompanied by the symmetry change $P112_1$ ($Z = 12$) $\longleftrightarrow$ $Cmc2_1$ ($Z = 4$).

The temperature dependence of the anomalous part $\delta n_i(T)$ of the birefringence of the crystal $SrMgF_4$ found by subtracting the extrapolated behavior of the birefringence of the orthorhombic phase from the dependences $\Delta n_i(T)$ (Fig. 3, curves *2* and *3*) is shown in Fig. 4. Both curves in Fig. 4 exhibit anomalies seen as sharp kinks below a temperature of 478 K. In addition, strong pre-transition birefringence "tails" are seen in the temperature interval $\Delta T \approx 60$ K above the main anomaly, which can mask both the character and temperature of the transition.

The anomalous part of birefringence measured in the orthorhombic setting is proportional to the square of the transition parameter and therefore reflects its temperature dependence: $\delta n(T) \propto \eta^2 \propto (T_0 - T)^{2\beta}$. Taking into account this relation, one can find the temperature dependence of the transition parameter $\eta(T)$, the exponent β and the transition temperature T_0, which fits this relation. Determining the transition temperature from the birefringence curves is problematic, especially when the transition is smeared out owing to some reasons. There are many ways of deter-

mining T_0. Based on our experimental results (Fig. 3), we used a simple method proposed in [8] of choosing the phase transition temperature from the straight lines $\delta n(T_0 - T)$ in the log—log scale shown in Fig. (5). The experimental points fit well the straight lines with $T_0 = 478$ K in the entire temperature range ($T_0 - T$) below the transition excluding a 10–15 K region near T_0. From the angle of the straight lines we find the temperature dependence of the transition parameter with the nonclassical exponent $2\beta = 0.65 \pm 0.01$. Thus, the transition temperature determined according to the method [8] agrees with the kink in the $\Delta n_i(T)$ curves. Therefore, taking into account the operational parameters of the Linkam TS 1500 heating stage, we conclude that the phase transition in $SrMgF_4$ occurs at $T_0 = 478 \pm 1$ K.

5. CONCLUSIONS

The present study has confirmed the presence of a phase transition in the $SrMgF_4$ crystal near $T_0 = 478$ K predicted in [7] ($T_c \approx 450$ K). However, we have found that the high-temperature phase of the crystal has orthorhombic symmetry rather than monoclinic one presumed in [7]. In addition, the phase transition is ferroelastic rather than ferroelectric. Since the volume of the unit cell exhibits multiplication at the transition, the latter can be regarded as improper ferroelastic transition. The component x_6 of spontaneous strain emerging below $T_0 = 478$ K is not linear in the transition parameter η. The phase transition occurs continuously, no jumps and temperature hysteresis of birefringence have been observed.

In our opinion, the thermal anomaly near $T \approx 1082$ K discovered in [6] results from decomposition of the chemical compounds and diffusion from the sample surface near the melting temperature ($T_{melt} = 1153$ K). The observed scatter of the experimental points in the measurements of $\Delta n_i(T)$ (Fig. 3) above $T = 1070$ K is caused by defects of the surface layer of the sample. As is seen in the view field of the microscope, the surface becomes uneven, wavy, and then loses transparency.

In conclusion, we have shown that, similar to all members of the $BaMF_4$ family (M = Mg, Mn, Fe, Co, Ni, Zn), the $SrMgF_4$ crystal at high temperatures belongs to the pyroelectric symmetry class $Cmc2_1$. Replacement of Ba by Sr in the inter-octahedron position does not change the symmetry of the crystal. On the other hand, the orthorhombic symmetry of $SrMgF_4$ is unstable and a transition to the monoclinic polar phase $P2_1$ occurs at $T_0 = 478$ K. The negative results of the investigation of the optical second harmonic in the $AMgF_4$ crystals (A = Sr, Eu, Sm) [4] can be explained by low values of the nonlinear optical coefficients, as in the case of $BaMgF_4$ [1]. The phase transition discovered in $SrMgF_4$ resembles in many respects the phase transitions observed in $BaMnF_4$ at $T_0 = 251$ K [3]. An improper ferroelastic phase transition with identical changes in the crystal system occurs in both crystals, and considerable contributions from the fluctuation of the order parameter are seen in the temperature ranges $(T_0 - T) < 15$ K and $(T - T_0) < 60$ K.

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