

MAGNETISM
AND FERROELECTRICITY

Optical Investigations of the Effect of Gradual Substitution
 $\text{NH}_4 \longrightarrow \text{Cs}$ on the Ferroelastic Phase Transition
in a CsLiSO_4 Crystal

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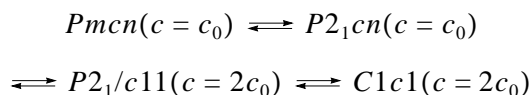
Abstract—Crystals of $\text{Cs}_x(\text{NH}_4)_{1-x}\text{LiSO}_4$ ($0.39 \leq x \leq 1.0$) solid solutions are grown and investigated using polarized light microscopy and measurements of the birefringence in the temperature range 100–530 K. The $(x-T)$ phase diagram of the $\text{Cs}_x(\text{NH}_4)_{1-x}\text{LiSO}_4$ solid solutions is constructed. It is demonstrated that, upon substitution of ammonium for cesium in the CsLiSO_4 crystal, the phase transition temperature gradually increases to such a degree that the ferroelastic phase can exist at room temperature. The triple point of intersection of the $Pm\bar{c}n$, $P2_1cn$, and $P112_1/n$ phase boundaries is determined. It is established that the introduction of ammonium in small amounts has an unusually strong effect on the refractive properties and character of the ferroelastic phase transition in the CsLiSO_4 crystal. © 2004 MAIK “Nauka/Interperiodica”.

1. INTRODUCTION

Crystals of the ALiSO_4 ($A = \text{K}, \text{NH}_4, \text{Rb}, \text{Cs}$) family contain LiO_4 and SO_4 tetrahedral groups that are linked into a framework structure of the tridymite type (cations A occupy large-sized holes). These crystals are convenient model objects for investigating phase transitions owing to the great diversity of phases and sequences of changes in the symmetry upon phase transitions. Moreover, structural transformations occurring in these materials are primarily associated with step-by-step orientational ordering of structural groups [1].

For crystals with a large-sized Cs^+ cation, namely, crystals of cesium lithium sulfate CsLiSO_4 , the initial structure with symmetry $Pm\bar{c}n$ ($c = c_0$) is most stable in the crystal family under investigation and is retained up to a temperature $T_{01} \approx 202$ K, at which the CsLiSO_4 crystal undergoes only one ferroelastic phase transition from the initial phase to the phase with monoclinic symmetry $P112_1/n$ ($c = c_0$) [2]. The unit cell parameters of this crystal at room temperature (293 K) are as follows: $a = 5.456$ Å, $b = 9.456$ Å, and $c = 8.820$ Å [2].

For crystals with a small-sized A^+ cation, namely, crystals of ammonium lithium sulfate NH_4LiSO_4 in the β modification [3], the initial phase becomes unstable at higher temperatures. During cooling, this compound undergoes the following sequence of phase transitions with a change in the initial symmetry:



at temperatures $T_1 = 460$ K, $T_2 = 284$ K, and $T_3 = 27$ K, respectively [4–6]. The phase is ferroelectric with con-

siderable spontaneous polarization at room temperature ($a = 5.28$ Å, $b = 9.14$ Å, $c = 8.786$ Å) [5] and ferroelastic below ~ 284 K.

Earlier [7], we showed that, in the concentration range $0 \leq x \leq 0.35$, $\text{Cs}_x(\text{NH}_4)_{1-x}\text{LiSO}_4$ crystals form a continuous series of solid solutions. An increase in the cesium content x leads to a gradual decrease in the phase transition temperatures T_1 and T_2 . However, the character of the high-temperature phase transition does not change [the critical exponent, which corresponds to the temperature dependence of the birefringence $(n_a - n_b)(T)$, remains constant and equal to $2\beta = 0.24 \pm 0.01$ for all compositions], even though the magnitudes of the birefringence and enthalpy anomalies decrease with an increase in the cesium content x in the crystal. As the cesium content increases, the low-temperature transition at $T = T_2$ becomes more similar to a first-order transition: the birefringence jump δn increases, and the temperature hysteresis ΔT becomes more pronounced. Moreover, according to the $(x-T)$ phase diagram [7], the region of existence of the ferroelectric phase is more extended at low contents x and the ferroelastic phase with symmetry $P2_1/c11$ disappears at $x > 0.22$. In this respect, it is important to determine the boundaries of the regions of the initial, ferroelectric, and ferroelastic phases with symmetries $Pm\bar{c}n$, $P2_1cn$, and $P112_1/n$, respectively.

In the present work, we continued our investigations of $\text{Cs}_x(\text{NH}_4)_{1-x}\text{LiSO}_4$ solid solutions in the concentration range $0.35 \leq x \leq 1.0$. For this purpose, we used polarized light microscopy and measurements of the birefringence of the crystals under investigation.

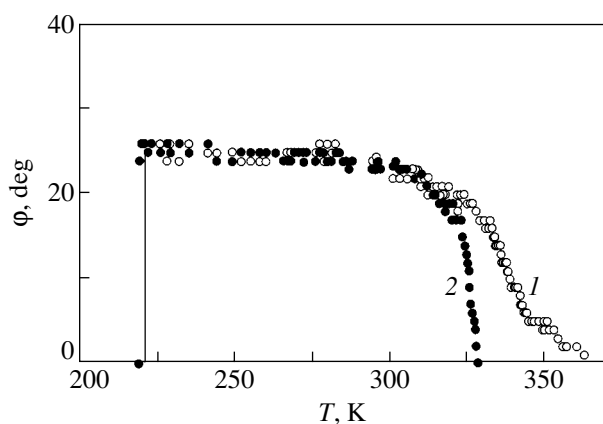


Fig. 1. Graph illustrating the influence of annealing on the temperature and character of the phase transition in a $\text{Cs}_x(\text{NH}_4)_{1-x}\text{LiSO}_4$ ($x=0.5$) solid solution according to the results of measurements of the rotation angle of the optical indicatrix $\varphi(T)$ with respect to the [001] direction: (1) prior to annealing and (2) after annealing.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Single crystals suitable for our experiments were prepared using two procedures described earlier in [7]. The quantitative composition of these crystals was determined by atomic absorption analysis. Crystals with a cesium content in the range $x = 0.35$ – 0.6 were grown from a mixture of NH_4LiSO_4 and CsLiSO_4 solutions in caustic ammonia taken in required proportion. Compounds with a cesium content in the range $x = 0.6$ – 1.0 were prepared through slow evaporation of the appropriate mixtures of NH_4LiSO_4 and CsLiSO_4 aqueous solutions at $T \approx 310$ K. For optical investigations, samples in the form of plates with different orientations and thicknesses were oriented using a URS-1 x-ray instrument. For the reasons given in [7], prior to optical and thermal investigations, the samples were necessarily annealed at a temperature of approximately 470 K for 2 h. The necessity of performing this annealing is illustrated in Fig. 1, which presents the results of measurements of the rotation angle of the optical indicatrix $\varphi(T)$ with respect to the [001] direction for a solid solution with $x = 0.5$ prior to and after annealing. For the sample not subjected to annealing, the phase transition temperature increases and inhomogeneous stresses arising in the crystal lead to a smearing of the observed anomaly, because, as was shown by Chekmasova *et al.* [8], the hydrostatic pressure substantially affects the phase transition temperature of the NH_4LiSO_4 crystal ($dT_1/dp = 90$ K/GPa). Upon annealing, the stresses are relieved and the dependence $\varphi(T)$ acquires a more perfect shape.

The crystal plates prepared were used in optical investigations and measurements of the birefringence from the (001) and (100) sections in the temperature range from 77 to ~ 500 K. The birefringence was mea-

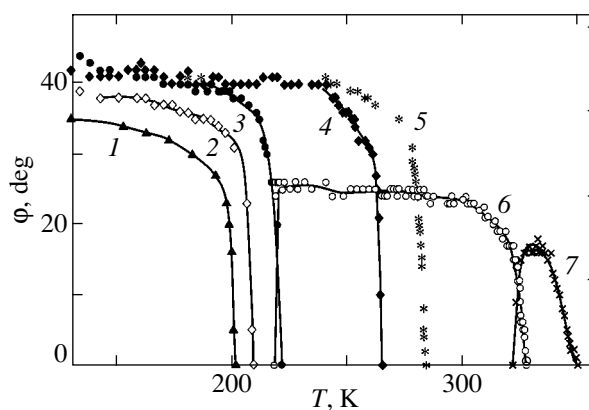


Fig. 2. Temperature dependences of the rotation angle of the optical indicatrix with respect to the [001] direction in $\text{Cs}_x(\text{NH}_4)_{1-x}\text{LiSO}_4$ crystals at cesium contents $x =$ (1) 1.00, (2) 0.95, (3) 0.90, (4) 0.80, (5) 0.71, (6) 0.5, and (7) 0.39.

sured on a Berek compensator with an accuracy of $\approx 10^{-5}$ and a Senarmont compensator with a sensitivity of no less than $\approx 10^{-7}$. The former compensator made it possible to examine small-sized samples and to determine the birefringence magnitude. The rotation angle of the optical indicatrix was measured using a polarizing microscope with an accuracy of $\pm 0.5^\circ$.

3. EXPERIMENTAL RESULTS

Observations of the single-crystal plates in polarized light revealed that crystals of all the studied compositions (in the corresponding temperature ranges) are characterized by a twin structure typical of the CsLiSO_4 ferroelastic phase. At temperatures below T_{01} , crystal plates of the (001) section have a streaky structure. The structural components differ in the extinction positions by an angle 2φ . The temperature dependences of the rotation angle of the optical indicatrix $\varphi(T)$ with respect to the [001] direction of a single twin are depicted in Fig. 2. Curve 1 represents the experimental data for pure cesium lithium sulfate CsLiSO_4 . A comparison of curves 1–5 shows that an increase in the ammonium content in the solid solution leads to a gradual displacement of the phase transition toward the high-temperature range. This is accompanied by an increase in the rotation angle of the optical indicatrix, but the phase transition, as before, proceeds in a gradual manner. For these compositions, the phase with monoclinic symmetry $P112_1/n$ is retained up to the liquid-nitrogen temperature. In the case of a solid solution with $x = 0.5$, i.e., when the ammonium content is equal to the cesium content (Fig. 2, curve 6), the phase transition temperature increases to such a degree that the monoclinic phase can exist already at room temperature; however, the stability region of the monoclinic phase becomes substantially narrower. Upon cooling in the tempera-

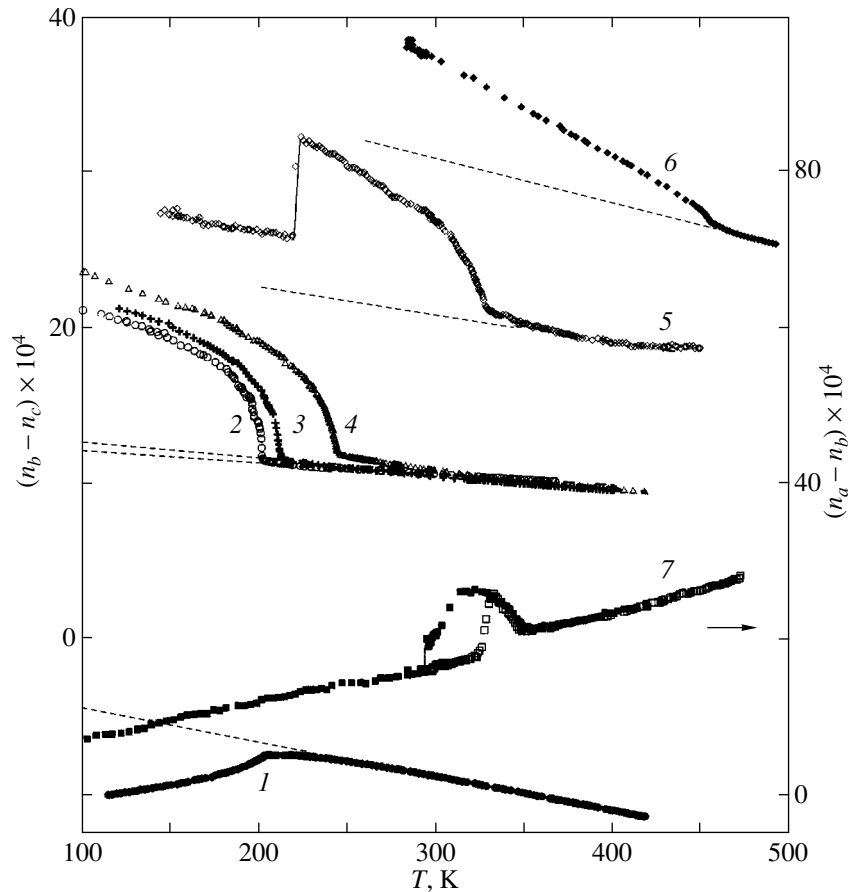


Fig. 3. Temperature dependences of the birefringence $(n_b - n_c)(T)$ for $\text{Cs}_x(\text{NH}_4)_{1-x}\text{LiSO}_4$ solid solutions at cesium contents $x = (1)$ 1.00, (2) 0.99, (3) 0.95, (4) 0.80, (5) 0.5, and (6) 0. (7) Temperature dependence of the birefringence $(n_a - n_b)(T)$ for the sample at $x = 0.39$ upon heating and cooling.

ture range close to the phase transition point $T_{02} \approx 220$ K, the magnitude of the rotation angle of the optical indicatrix drastically decreases to zero and the crystal again transforms into the orthorhombic phase. For the sample at a cesium content $x = 0.39$ (Fig. 2, curve 7), the phase with monoclinic symmetry $P112_1/n$ is observed only in a narrow temperature range (~ 25 K). The thermal investigations of the second optical harmonic in samples at cesium contents $x = 0.5$ and 0.39 revealed that the crystal has a center of symmetry (the second optical harmonics is absent) at temperatures above $T = T_{02}$ and is characterized by the 2ω generation below this temperature. As a result, the crystal loses the center of symmetry and transforms into the phase with an orthorhombic polar group.

The results of investigations into the temperature dependences of the birefringence $\Delta n_a = (n_b - n_c)$ for $\text{Cs}_x(\text{NH}_4)_{1-x}\text{LiSO}_4$ solid solutions with different cesium contents x are presented in Fig. 3. These data also indicate a gradual displacement of the phase transition toward the high-temperature range with an increase in the ammonium content in the material. Moreover, it is found that the substitution $\text{NH}_4 \rightarrow \text{Cs}$

strongly affects the refractive properties of the CsLiSO_4 crystal. The introduction of small amounts of ammonium into the CsLiSO_4 compound radically changes the optical indicatrix. As a result, the birefringence Δn_a reverses sign. It is known that the refractive indices of the initial crystals are in the following proportions: $n_c > n_b$ for the CsLiSO_4 crystal [9] and $n_b > n_c$ for the NH_4LiSO_4 crystal [10]. Indeed, as can be seen from Fig. 3, the birefringence $\Delta n_a = (n_b - n_c)$ is negative for pure CsLiSO_4 (curve 1) and positive for pure NH_4LiSO_4 (curve 6). The introduction of 1 mol % NH_4^+ into the CsLiSO_4 compound leads to a change in the sign of the birefringence Δn_a and affects the temperature dependence of Δn_a (Fig. 3, curve 2). A further increase in the ammonium content in the crystal affects only the phase transition temperature (Fig. 3, curves 3–5). For a cesium content $x = 0.5$ (Fig. 3, curve 5), the crystal undergoes the second phase transition at a temperature $T_{02} \approx 220$ K, which is attended by a jump in the birefringence. For comparison, curve 6 in Fig. 3 shows the temperature dependence of the birefringence Δn_a for

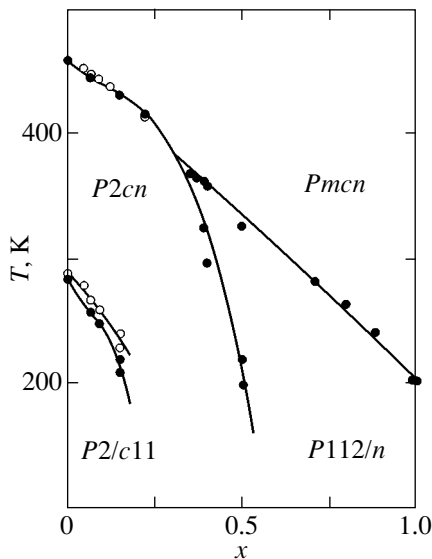


Fig. 4. Phase (x - T) diagram of the $\text{Cs}_x(\text{NH}_4)_{1-x}\text{LiSO}_4$ solid solutions according to the DSC data obtained upon heating [7] (open circles) and the results of optical investigations upon cooling (closed circles).

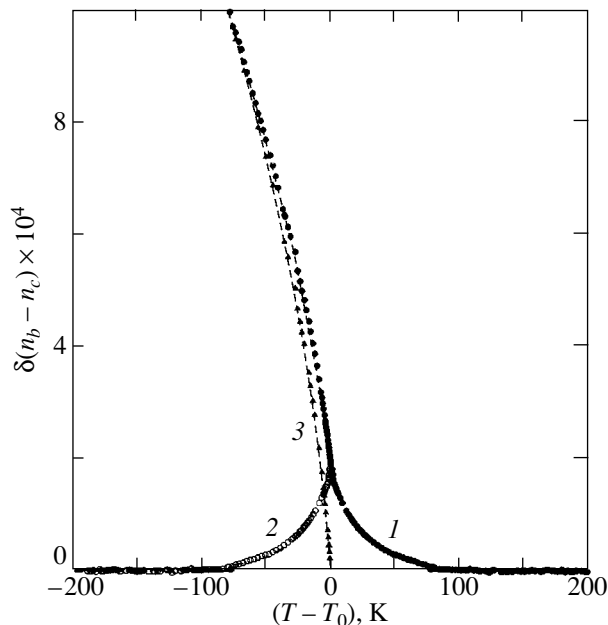


Fig. 5. (1) Anomaly of the birefringence of the CsLiSO_4 crystal and the decomposition of this anomaly into (2) the fluctuation component and (3) the component associated with the parameter of the phase transition.

pure NH_4LiSO_4 upon the phase transition $Pmcn \rightleftharpoons P2_1cn$.

Solid solutions with a cesium content $x = 0.39$ were examined using a crystal plate of the (001) section (Fig. 3, curve 7). The temperature dependence $(n_a - n_b)(T)$, like the dependence $\varphi(T)$, is characterized by

two special points that correspond to two phase transitions. The high-temperature transformation observed at a temperature T_{01} exhibit features specific to second-order phase transitions. The birefringence jump and pronounced temperature hysteresis ($\Delta T \approx 30$ K) observed at a temperature T_{02} indicate that this transformation is a first-order phase transition.

4. DISCUSSION

The phase diagram of the $\text{Cs}_x(\text{NH}_4)_{1-x}\text{LiSO}_4$ solid solutions (Fig. 4) was constructed according to the results of optical investigations performed in this work and data obtained earlier in [7]. As can be seen from Fig. 4, the dependence of the instability temperature of the initial phase on the cesium content in the solid solution exhibits a nearly linear behavior. The end points of this dependence correspond to the CsLiSO_4 and NH_4LiSO_4 compounds. The compositions with cesium contents $x \approx 0.4$ are characterized by a triple point at which the $Pmcn$, $P2_1cn$, and $P112/n$ phases coexist. The quantity dT_{02}/dx for the $P112/n$ - $P2_1cn$ phase boundary is considerably larger than that for the other phase boundaries.

The temperature dependence of the anomalous component of the birefringence of the CsLiSO_4 crystal in the range below the phase transition temperature T_{01} is plotted in Fig. 5. This dependence was obtained by subtracting the linear dependence of the birefringence (extrapolated from the initial phase) from the dependences depicted in Fig. 3. As can be seen, the pretransition effects are observed over a wide temperature range (≈ 100 K) above the phase transition temperature. Similar effects were revealed earlier in the temperature dependences of the lattice parameters and in the heat capacity curve [11]. At temperatures close to T_{01} , the anomalous component of the birefringence governed by the pretransition phenomena reaches 20% of the total anomaly. For this reason, the phase transition temperature and the birefringence anomaly associated with the parameter of the phase transition below T_{01} cannot be determined from the temperature dependence of the birefringence Δn_a . The fluctuation contribution of the transition parameter to the birefringence can be excluded, by analogy with [12], under the assumption that the temperature dependence of the fluctuation component of the birefringence anomaly above and below the phase transition temperature is symmetric with respect to the T_{01} temperature. The decomposition of the birefringence anomaly near T_{01} into the fluctuation component and the component associated with the transition parameter (δn_a) for the CsLiSO_4 crystal is illustrated in Fig. 5. The temperature dependence of the latter component on a logarithmic scale makes it possible to determine the critical index of the temperature behavior of the transition parameter. Making allowance for the fact that the anomalous component of the birefringence measured in the orthorhombic setting is proportional to the transition parameter squared, i.e.,

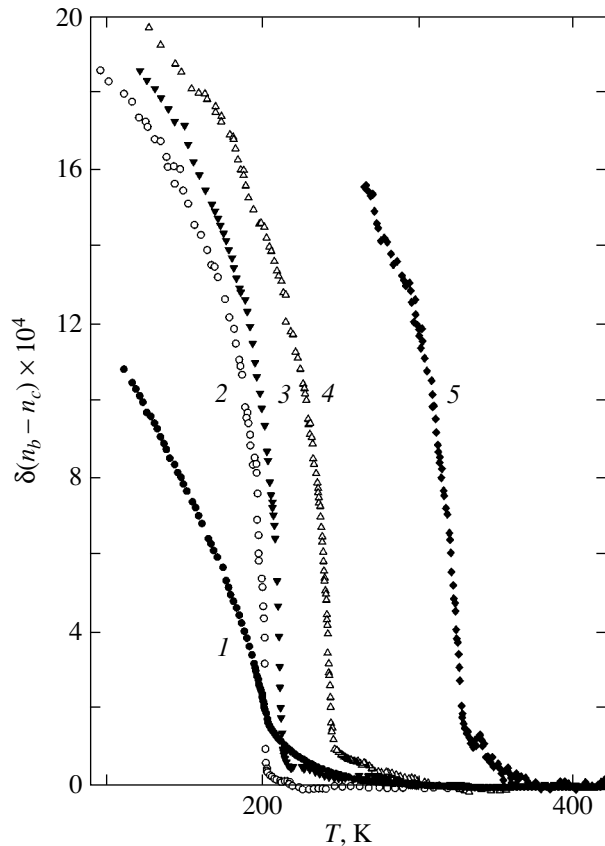


Fig. 6. Temperature behavior of the anomalous component of the birefringence in the ferroelastic phase of $\text{Cs}_x(\text{NH}_4)_{1-x}\text{LiSO}_4$ crystals at cesium contents $x = (1)$ 1.00, (2) 0.99, (3) 0.95, (4) 0.80, and (5) 0.5.

$\delta n_a(T) \sim \eta^2 \sim (T_0 - T)^{2\beta}$, we determine the “nonclassical” critical index $\beta = 0.38 \pm 0.01$. The nonclassical magnitude of the critical index can be explained by the closeness of the phase transition to the Landau tricritical point. In this case, the term with η^6 must be taken into account in the expansion of the thermodynamic potential because of the smallness of the coefficient of η^4 . In actual fact, the results of calculations performed according to the procedure described in [13] demonstrated that all experimental points of the curve $\delta n_a(T)$ fall on a linear curve $\Delta T/\delta n \sim \delta n$. The phase transition point is found to be close to the tricritical point (second-order phase transitions), and the quantity $(T_c - T_0)$ is the measure of closeness to the point T_c (in our case, this difference is equal to 1.1 K).

The introduction of small amounts of ammonium (1 mol %) into the initial compound CsLiSO_4 brings about a drastic decrease in the pretransition effects and a change in the shape and magnitude of the birefringence anomaly (Fig. 6). With a further increase in the content x , the birefringence “tail” associated with the pretransition phenomena increases progressively but the shape and magnitude of the birefringence anomaly in the distorted phase remain unchanged. The critical

index β was determined from the dependence $\delta n_a(T)$ plotted on a logarithmic scale. For all compositions with $x \neq 1$, the critical index proved to be equal to $\beta = 0.25 \pm 0.01$. Moreover, the linear relationship $(\delta n_a)^2 \sim \eta^4 \sim T - T_{01}$ is satisfied within a temperature range 60 K below the phase transition point. This indicates that, in the solid solutions under investigation, the phase transition corresponds to the Landau tricritical point and that the coefficient of the term with η^4 in the expansion of the thermodynamic potential is equal to zero.

5. CONCLUSIONS

Thus, the results of the above investigations demonstrated that the substitution of even small amounts of ammonium for cesium in the cesium lithium sulfate compound substantially affects the optical characteristics of the material and the character of the phase transition; however, the ferroelastic nature of the phase transition remains unchanged. The assumption was made that the observed change in the optical properties is most likely associated with the specific features of the molecular ion NH_4^+ introduced into the initial compound. It should also be noted that our earlier investigations [14], in which the atomic cation Rb^+ was substituted for the Cs^+ ion, did not reveal radical changes in either the optical properties of the crystal or the character of the phase transition.

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REFERENCES

1. K. S. Aleksandrov and B. V. Beznosikov, *Structural Phase Transitions in Crystals (The Potassium Sulfate Family)* (Nauka, Novosibirsk, 1993).
2. A. I. Kruglik, M. A. Simonov, and E. P. Zhelezin, Dokl. Akad. Nauk SSSR **247** (7), 1384 (1979) [Sov. Phys. Dokl. **24**, 596 (1979)].
3. S. V. Mel'nikova, A. V. Kartashev, V. A. Grankina, and I. N. Flerov, Fiz. Tverd. Tela (St. Petersburg) **45** (8), 1497 (2003) [Phys. Solid State **45**, 1572 (2003)].
4. A. I. Kruglik, M. A. Simonov, and K. S. Aleksandrov, Kristallografiya **23**, 494 (1978) [Sov. Phys. Crystallogr. **23**, 274 (1978)].
5. K. Itoh, H. Ishikuta, and E. Nakamura, Acta Crystallogr. B **37**, 664 (1981).
6. A. Dollase, Acta Crystallogr. B **25**, 2298 (1969).
7. S. V. Mel'nikova, V. A. Grankina, and A. V. Kartashev, Fiz. Tverd. Tela (St. Petersburg) **44** (2), 365 (2002) [Phys. Solid State **44**, 379 (2002)].
8. T. I. Chekmasova, I. S. Kabanov, and V. I. Yusvak, Phys. Status Solidi A **44**, K155 (1977).

9. A. T. Anistratov, A. V. Zamkov, L. A. Kot, *et al.*, *Fiz. Tverd. Tela (Leningrad)* **24** (9), 2763 (1982) [*Sov. Phys. Solid State* **24**, 1565 (1982)].
10. A. T. Anistratov and S. V. Mel'nikova, *Izv. Akad. Nauk SSSR, Ser. Fiz.* **39** (4), 808 (1975).
11. K. S. Aleksandrov, L. I. Zhrebtsova, I. M. Iskornev, *et al.*, *Fiz. Tverd. Tela (Leningrad)* **22**, 3673 (1980) [*Sov. Phys. Solid State* **22**, 2150 (1980)].
12. F. J. Schäfer and W. Kleeman, *J. Appl. Phys.* **57**, 2606 (1985).
13. S. V. Mel'nikova, I. N. Flerov, and A. T. Anistratov, *Fiz. Tverd. Tela (Leningrad)* **23** (12), 3570 (1981) [*Sov. Phys. Solid State* **23**, 2074 (1981)].
14. S. V. Melnikova, A. D. Vasiliev, V. A. Grankina, *et al.*, *Ferroelectrics* **170**, 139 (1995).

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