
LATTICE DYNAMICS
AND PHASE TRANSITIONS

Specific Features of the Ferroelastic Phase Transition in $\text{CsLiS}_{1-z}\text{Cr}_z\text{O}_4$ Solid Solutions

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Abstract—Single crystals of the $\text{CsLiS}_{1-z}\text{Cr}_z\text{O}_4$ solid solutions ($z = 0, 0.1, 0.4, 0.5, 0.9, 1.0$) are grown, optical polarization studies are performed, and the birefringence and the angle of rotation of the optical indicatrix $\varphi(T)$ are measured. A $(z-T)$ phase diagram is constructed in the temperature range from 77 to ~ 550 K. It is established that substitution of chromium for sulfur has practically no effect on the shape of the optical indicatrix in the initial phase with $Pm\bar{c}n$ symmetry but produces strong distortions in the monoclinic phase with $P112_1/n$ symmetry. The unusual shape of the curve $\varphi(T)$ for compositions with $z \approx 1$ is accounted for by the interaction of the polarization-constant tensor components a_{ij} . No radical differences in the patterns of the ferroelastic phase transition between CsLiSO_4 and CsLiCrO_4 are revealed (the critical exponent for the transition parameter is $\beta = 0.33 \pm 0.01$). These crystals differ only in the magnitudes of the anomalies, which is associated with the large difference between the ionic radii of sulfur and chromium.

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1. INTRODUCTION

Crystals of cesium sulfate CsLiSO_4 and cesium chromate $\beta\text{-CsLiCrO}_4$ [1] have a tridymite-type framework structure and undergo phase transformations with the same change in symmetry: $Pm\bar{c}n \rightleftharpoons P112_1/n$. The phase transitions in these compounds ($T_0 = 201$ K for CsLiSO_4 and 427 K for CsLiCrO_4) are driven by ordering of the $\text{S}(\text{Cr})\text{O}_4$ tetrahedral groups [2–6]. The change in the symmetry suggests that both crystals belong to the class of proper ferroelastics, for which the transition order parameter η is related linearly to the spontaneous deformation x_s [6]. Below the phase transition point, a shear deformation component x_6 appears and the optical indicatrix rotates through an unusually large angle ($\varphi \sim 30^\circ\text{--}40^\circ$) about the [001] direction [3, 5]. It is believed that the shear deformation component x_6 , the angle of rotation of the optical indicatrix φ , and the monoclinic angle $\Delta\gamma(T)$ appearing below the phase transition region should in this case behave in the same way with variations in temperature.

However, It is known that, in the CsLiSO_4 compound, the spontaneous deformation $x_6(T)$ [7] derived from the dependence $\Delta\gamma(T)$ [5] and the angle of rotation of the optical indicatrix $\varphi(T)$ have different but smooth temperature dependences characteristic of second-order phase transitions. The dependences $\Delta\gamma(T)$ and $\varphi(T)$ obtained from experiment for CsLiCrO_4 follow an unusual pattern [3]. The monoclinic angle appears at the phase transition, and it increases with decreasing temperature and then decreases to zero. At $T = 130$ K,

we have $\Delta\gamma = 0$. As the temperature decreases, this quantity reverses sign. The angle of rotation of the indicatrix φ depends in a different way on temperature. At temperatures close to the phase transition point (in the range $T - T_0 \approx 15$ K), this angle increases rapidly from zero to 39° and then gradually decreases to 25° [3].

To account for the different behavior of the spontaneous deformation and the angle of rotation of the indicatrix in CsLiSO_4 with variations in temperature, the ferroelastic phase transition was assumed [8] to be of pseudoproper character, with one parameter η related linearly to the shear deformation component x_6 .

Attempts were made also to analyze the reasons for the unusual behavior of the monoclinic angle in cesium chromate [3, 8]. To find an explanation for the specific features in the behavior of the physical properties of this crystal, a two-sublattice model was proposed [8] for a pseudoproper ferroelastic phase transition with two parameters exhibiting different temperature dependences. One of these parameters is connected with the chromium sublattice, and the other, with the sublattice of cesium atoms. The resultant spontaneous deformation x_6 has an unusual temperature dependence. By contrast, the authors of [3] tend to believe that, owing to the strong structural distortions (see table), the shear deformation in CsLiCrO_4 in the ferroelastic phase contains two contributions, namely, a contribution associated with the appearance of a transition parameter and another one associated with thermal expansion.

We report here on a study of the effect of gradual $\text{S} \rightarrow \text{Cr}$ substitution on the temperature and character

of the ferroelastic phase transition in the CsLiSO_4 – CsLiCrO_4 system.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Our study involved optical polarization and birefringence measurements. Single crystals of the $\text{CsLiS}_{1-z}\text{Cr}_z\text{O}_4$ solid solutions were grown by the Bridgman method in platinum ampoules placed in a vertical tubular furnace with an axial temperature gradient of 12–15 K/cm and a pulling rate of 0.8 mm/h. The initial materials used for the preparation of the solid-solution single crystals were CsLiSO_4 and CsLiCrO_4 crystals synthesized from sulfates and chromates and grown subsequently by the Bridgman method. The composition of the materials was checked using atomic absorption analysis. The optical polarization studies and birefringence measurements were performed on plates of the (001) cut in the temperature range extending from 77 to ~550 K. The angle of rotation of the optical indicatrix was determined with a polarizing-light microscope to an accuracy of $\pm 0.5^\circ$. The birefringence was measured with a Berek compensator with an accuracy of $\approx 10^{-5}$. Because of the large ($\sim 35^\circ$) rotation of the optical indicatrix, the experiments in the monoclinic phase included careful orientation of the position of the extinction of the sample at each temperature point.

3. EXPERIMENTAL RESULTS

Studies of the $\text{CsLiS}_{1-z}\text{Cr}_z\text{O}_4$ solid solutions revealed the presence of a twin structure characteristic of the CsLiSO_4 and CsLiCrO_4 ferroelastic phases for all compositions (in the corresponding temperature ranges). A stripe structure with components differing in the positions of extinction by an angle of 2φ becomes visible in plates of the (001) cut below T_0 . The temperature dependences of the angle of rotation of the optical indicatrix $\varphi(T)$ about the [001] axis in a particular twin are shown graphically in Fig. 1. Curve 1 represents experimental data for CsLiSO_4 , and curve 6, for CsLiCrO_4 . A comparison of curves 1–6 shows that an increase in the chromium content in the solid solution brings about a gradual shift of the phase transition toward high temperatures. This is accompanied by a slight increase in the angle of rotation of the optical indicatrix as well, but the phase transition remains smooth. The increase in the angle φ is proportional to the change in the angle of rotation of the tetrahedral groups (see table). The variation of the curve $\varphi(T)$ in shape is noteworthy. The unusual behavior of the angle of rotation of the optical indicatrix in CsLiCrO_4 with variations in temperature smoothens out gradually as the chromium content in the crystal decreases.

The results of the measurements of the birefringence $\Delta n_c(T)$ of the solid solutions are presented in

Optical and structural parameters of CsLiSO_4 and CsLiCrO_4 crystals at $T_0 - T = 100$ K

Parameters of the crystals	CsLiSO_4	CsLiCrO_4
Angle of rotation of the T groups, deg	$10\uparrow$ [2]	$18\uparrow$ [3]
Cs atomic displacement, Å	$0.02\uparrow$ [2]	$0.09\downarrow$ [3]
$\Delta\gamma$, deg	0.29 [2]	max. 0.5 [3, 8]
φ , deg	37	27
Δn_c	0.003	0.014
x_6 (experiment)	0.0055 [7]	$x_6^1 = 0.02$, $x_6^2 = -0.01$ [8]
x_6 (calculation)	0.01	0.05

Note: Arrows indicate that oxygen and cesium atoms are displaced in phase in cesium sulfate and out of phase in cesium chromate.

graphical form in Fig. 2. Samples with different chromium contents exhibit practically the same temperature dependence $\Delta n_c(T)$ in the orthorhombic phase because of the thermal expansion of the material. The birefringence of samples of all concentrations z passes through zero and reverses sign in the temperature range from 370 to 470 K. The substitution of chromium for sulfur has only an insignificant effect on the absolute magnitude of the birefringence. Below the phase transition point, one observes not only a large rotation of the indicatrix but also a substantial increase in the birefringence. Indeed, in pure CsLiCrO_4 , the birefringence increases by more than one order of magnitude as compared to that in CsLiSO_4 . The differences between the refractive indices Δn_c for compositions with $0 < z < 1$ are intermediate in magnitude. Thus, the replacement of sulfur ions by larger chromium ions brings about

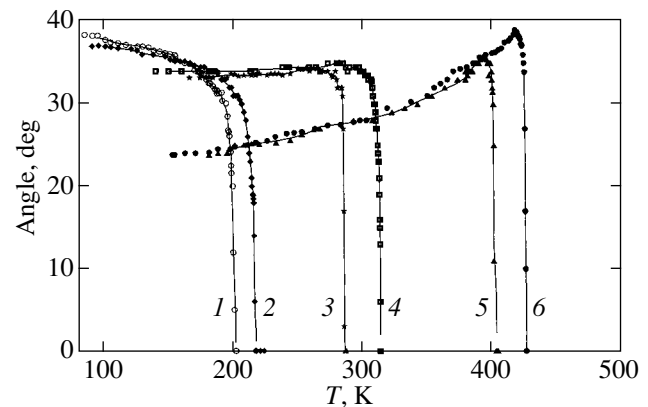


Fig. 1. Rotation of the optical indicatrix relative to the [001] direction in the monoclinic phase of $\text{CsLiS}_{1-z}\text{Cr}_z\text{O}_4$ crystals at different chromium contents: $z = (1) 0$, $(2) 0.1$, $(3) 0.4$, $(4) 0.5$, $(5) 0.9$, and $(6) 1.0$.

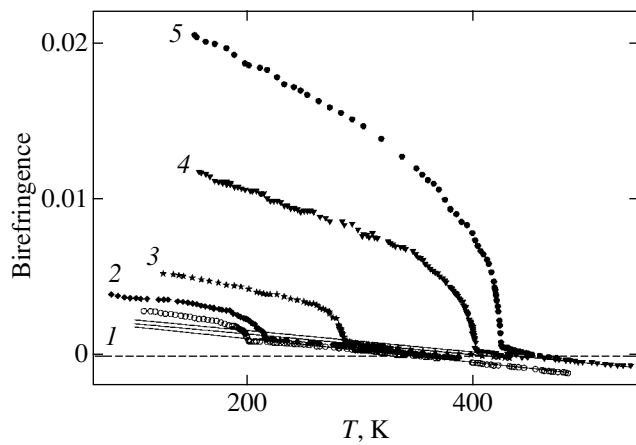


Fig. 2. Temperature dependences of the birefringence $\Delta n_c = (n_m - n_p)$ of the $\text{CsLiS}_{1-z}\text{Cr}_z\text{O}_4$ solid solutions at different chromium contents: $z = (1) 0, (2) 0.1, (3) 0.4, (4) 0.9,$ and $(5) 1.0$.

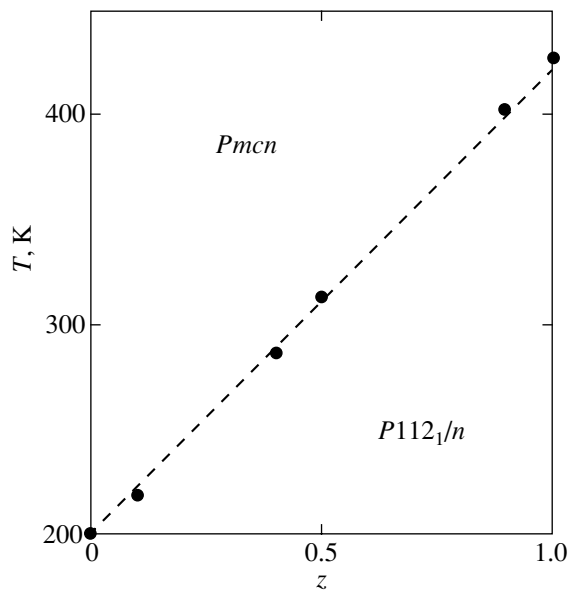


Fig. 3. The z - T phase diagram of the $\text{CsLiS}_{1-z}\text{Cr}_z\text{O}_4$ solid solutions.

large deformations of the crystal and strong distortions of the indicatrix in the monoclinic phase.

Figure 3 presents the (z - T) phase diagram of the solid solutions studied, which was constructed on the basis of the above experiments. The temperature of stability of the orthorhombic phase is seen to depend linearly on the sulfur-to-chromium concentration ratio in the material. As the S^{6+} ions ($R \approx 0.12 \text{ \AA}$) are gradually replaced by the larger Cr^{6+} ions ($R \approx 0.30 \text{ \AA}$), the temperature of stability of the initial phase increases. No new phase boundaries are observed in the (z - T) diagram.

4. DISCUSSION OF THE RESULTS

The birefringence measurements with the Berek compensator were always performed in the direction of the principal axes of the optical indicatrix. One uses plates cut in the (001) plane of CsLiSO_4 to determine the refractive index difference $\Delta n_c = (n_m - n_p)$ at room temperature [9]. The birefringence is equal to the difference between the refractive indices $\Delta n_c = (n_m - n_p) = (n_b - n_a)$ only in the orthorhombic phase, in which the principal axes of the optical indicatrix coincide with the axes of the unit cell. In the monoclinic phase of the crystals, the optical indicatrix rotates so that $\Delta n_c = (n_m - n_p) \neq (n_b - n_a)$. The measurements of the dependences $\Delta n_c(T)$ (Fig. 2) have to be performed on samples whose orientation is properly adjusted at each temperature point. In this case, the experimental curve reveals a complex dependence on the transition parameter: $\Delta n_c \sim A\eta + B\eta^2$ [3].

By transforming the tensor of polarization constants a_{ij} to the reference frame that changes its orientation with temperature, we obtain

$$\Delta n_c = n^3 a_6 / \sin 2\varphi = n^3 p_{66} x_6 / \sin 2\varphi,$$

where n is the averaged refractive index and p_{66} is the coefficient of elasto-optical effect. This suggests that the deformation should be related to the angle of rotation of the optical indicatrix through a complex relationship, $x_6 \sim \Delta n_c \sin 2\varphi$. For small angles of rotation of the indicatrix and weak temperature-induced birefringence variations, one may expect the proportionality $x_6(T) \sim \varphi(T)$, as in the case of RbMnCl_3 [10]. In CsLiSO_4 , the angle of rotation of the indicatrix is large and, therefore, the dependence $\varphi(T)$ does not reflect the behavior of $x_6(T)$ [7]. In CsLiCrO_4 , one observes, besides a large angle of rotation of the indicatrix, a strong variation of the birefringence in the phase transition region, because it reverses sign in this crystal slightly above the phase transition point and increases rapidly thereafter to $\Delta n_c = 0.02$ (Fig. 2).

Figure 4 plots the dependences $\Delta n_c \sin 2\varphi(T)$ for all the crystals studied. Although the angle of rotation of the indicatrix is a composite function, the curves are smooth. By replotting them on a log scale, one can determine the critical exponent β for the transition parameter. Its value turned out to be the same for all compositions: $\beta = 0.33 \pm 0.01$. This value of the exponent in the temperature dependence of the transition parameter fits the results of our measurements of the birefringence $\Delta n_c(T)$ in CsLiSO_4 [11] and CsLiCrO_4 [3], which were performed by the Senarmont method in the initial cell geometry, where the anomalous part of the birefringence $\delta n_a \sim B\eta^2$. Thus, for a proper ferroelastic phase transition, one can find the shear deformation $x_6 = \Delta n_c \sin 2\varphi / n^3 p_{66}$ by measuring the change in the birefringence and angle of rotation of the indicatrix with variations in temperature. The absolute value of x_6

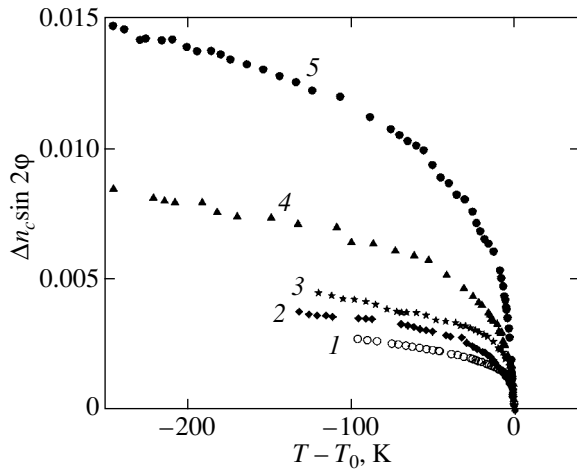


Fig. 4. Dependences $\Delta n_c \sin 2\varphi(T)$ for $\text{CsLiS}_{1-z}\text{Cr}_z\text{O}_4$ samples at different chromium contents: $z = (1) 0, (2) 0.1, (3) 0.4, (4) 0.9, \text{ and } (5) 1.0$.

calculated in this way for CsLiSO_4 with the use of $p_{66} = 0.05$ [7] and of the average refractive index $n_{\text{av}} \approx 1.54$ [9] is, however, almost twice the experimental values [7]. This implies that the anomalies of the refractive indices in this crystal are caused not only by the appearing component of the shear deformation x_6 but also by a contribution from the transition parameter η .

Using, with considerable reservations, the same values of the constants $p_{66} = 0.05$ and $n_{\text{av}} \approx 1.54$ for CsLiCrO_4 , for the x_6 deformation, we also obtain a value twice the experimental result under the assumption that the spontaneous deformation is a sum of the absolute contributions due to both sublattices, namely, $x_6 = |x_6^1| + |x_6^2|$ [8]. Figure 5 plots the temperature dependences of the shear deformation component, $x_6(T)$, calculated in this way and the experimental data obtained for CsLiSO_4 and CsLiCrO_4 [7, 8]. We readily see that, while the experimental and calculated curves for the two crystals are similar in character, they differ in the value of x_6 by a factor of 2.

5. CONCLUSIONS

The replacement of the S^{6+} ion ($R \approx 0.12 \text{ \AA}$) with a larger Cr^{6+} ($R \approx 0.30 \text{ \AA}$) in the $\text{CsLiS}_{1-z}\text{Cr}_z\text{O}_4$ system brings about a substantial increase in the temperature of stability of the initial phase. The phase transition temperature T_0 depends linearly on the chromium percentage in the compound. No new boundaries were found in the phase diagram.

The substitution of chromium for sulfur has practically no effect on the shape of the optical indicatrix in the initial phase. In the monoclinic phase, the $\text{S} \rightarrow \text{Cr}$ replacement brings about large changes in the deformation and rotation components a_{ij} of the polarization

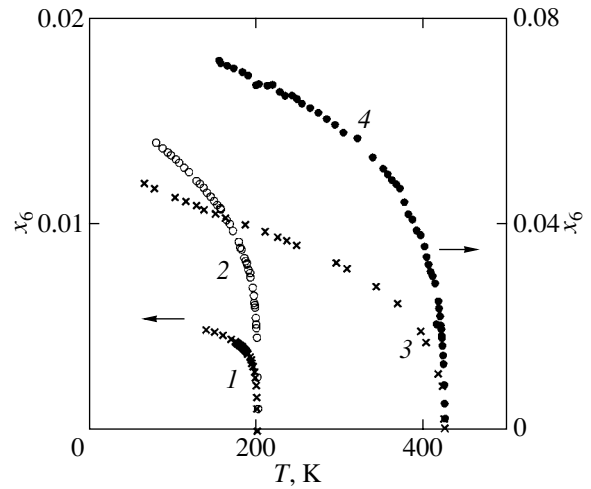


Fig. 5. (1, 3) Experimental [7, 8] and (2, 4) calculated (in this work) temperature dependences of the shear deformation component $x_6(T)$ for (1, 2) CsLiSO_4 and (3, 4)

CsLiCrO_4 crystals. (3) The sum of absolute values $|x_6^1| + |x_6^2|$ [8].

constant tensor. The experimental results suggest the $\text{S}(\text{Cr})\text{O}_4$ tetrahedra to play a dominant role in the ordering processes.

The interaction between the tensor components a_{ij} accounts for the change in the shape of the curve $\varphi(T)$ for compositions with a high chromium content. The anomalous part of the birefringence $\delta n_c(T)$, which appeared below the phase transition region, increases gradually with increasing chromium content and, in pure CsLiCrO_4 , become 10 times larger than that in CsLiSO_4 . Despite the substantial difference in the behavior of the optical properties in solid solutions with variations in temperature, the phase transition retains its character: $\beta = 0.33 \pm 0.01$.

The appearance of shear deformation is accompanied by a strong elasto-optical effect. The calculations performed using the relationship $x_6 = \Delta n_c \sin 2\varphi / n^3 p_{66}$, where $p_{66} = 0.05$ [7] and $n_{\text{av}} \approx 1.52$ [5], yield a result exceeding the experimental data obtained for CsLiSO_4 [7] and CsLiCrO_4 [8] by a factor of 2.

The studies of the behavior of the optical properties of solid solutions with variations in temperature did not reveal any radical differences between the cesium sulfate and cesium chromate. These crystals differ only in the magnitude of the anomalies accompanying the phase transition, which is certainly associated with the large difference between the ionic radii of sulfur and chromium. As follows from the calculations, the anomalies in the optical properties accompanying the phase transitions in CsLiSO_4 and CsLiCrO_4 cannot be described by the photoelastic effect through the shear deformation alone. There is a contribution from a tran-

sition order parameter (single- or two-component) which is related linearly to the spontaneous deformation.

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