
Thermal Expansion and Phase Transformation Observation in Cs₂BX₄ (B=Hg, Cd; X=Br, Cl) Crystals

2. Cs₂HgBr₄ and Cs₂CdBr₄ crystals

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Abstract

Photoelastic and acoustooptic (AO) parameters of Cs₂HgBr₄ and Cs₂CdBr₄ crystals are determined on the basis of studies for thermal expansion and optical indicatrix rotation at the ferroelastic (Fel) phase transition (PT) and the direct piezooptic measurements. It is shown that Cs₂HgBr₄ and Cs₂CdBr₄ crystals are good AO materials. Their photoelastic coefficients achieve respectively the values of $p_{44}=0.12$ and $p_{44}=0.2$, while the AO figures of merit are $M_2=126.5 \times 10^{-15} \text{ s}^3/\text{kg}$ for Cs₂HgBr₄ and $M_2=366.9 \times 10^{-15} \text{ s}^3/\text{kg}$ for Cs₂CdBr₄ crystals. From the obtained results it follows that, in both Cs₂HgBr₄ and Cs₂CdBr₄, the PT to the Fel phase $2/m$ is a first-order improper one, whereas the PT into the triclinic phase is of a second order. The orientations of domain walls in the Fel phase and the phase boundary between the incommensurate and Fel phases are determined.

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Key words: optical indicatrix, incommensurate structure, domain structure, thermal expansion.

Introduction

It has been reported by *Kityk et. al.* [1] that Cs₂HgCl₄ crystals exhibit a high value of acoustooptic (AO) figure of merit (FM) M_2 . These crystals (as well as, probably, Cs₂HgBr₄ and Cs₂CdBr₄ crystals) are transparent in a wide spectral range (0.3-15 μm) [1]. In order to calculate the AO FM,

$$M_2 = \frac{n^6 p_{ef}^2}{\rho v^3}, \quad (1)$$

one has to know all the parameters which are included into Eq. (1), i.e. the refractive indices n , the photoelastic (PhEl) coefficients p_{ef} , crystal density ρ and the ultrasonic velocity v . As a matter of fact, the ultrasonic velocity has just the most essential effect on the M_2 magnitude and it should be therefore as low as possible. The relevant values, characteristic for the above

crystals, are indeed quite low [2,3]. Nevertheless, one should also measure the three other parameters in Eq. (1), in particular the PhEl coefficients. The latter have been determined earlier with the interferometric technique only for Cs₂HgCl₄ crystals [1]. We conclude from the results presented in [2,3] that it is the transverse ultrasonic waves in Cs₂HgBr₄ and Cs₂CdBr₄ crystals, which exhibit the lowest velocities. The corresponding values for the transverse waves are $v_t=804.9\text{m/s}$ in case of Cs₂HgBr₄ and $v_t=843\text{m/s}$ in case of Cs₂CdBr₄ crystals [3]. Then the efficiency of AO interaction should depend upon the elasto-optic coefficient p_{44} . For the proper ferroelastics (Fel), these coefficients may be evaluated from the temperature dependences of optical indicatrix rotation induced by spontaneous deformation (SD) and thermal expansion in the Fel phase (the point

group $2/m$). It should be noted that both crystals exhibit the Fel phase transition (PT). The whole sequences of structural phases according to the literature are presented in Table 1.

The present paper is devoted to determination of PhEl coefficients for Cs₂BX₄ (B=Hg, Cd; X=Br, Cl) crystals and estimation of AO FM on the basis of optical indicatrix rotation studies and thermal expansion measurements.

Experimental

The crystals of Cs₂BX₄ (B=Hg, Cd; X=Br, Cl) were grown with the Bridgman technique. Their thermal expansion was studied with the aid of the capacity dilatometer (the sensitivity of 2 nm) in both cooling and heating runs (the temperature rate $\partial T/\partial t=1\text{K/min}$). The phase transformations were observed with the optical polarization microscope equipped with cooling cell. The accuracy for determination of optical indicatrix orientation was $\pm 0.5\text{deg}$. In addition, the piezoptic coefficients were measured at the room temperature, basing on the optical indicatrix rotation around X axis under the influence of mechanical stress σ_4 .

Results and discussion

a) Cs₂HgBr₄ crystals

As seen from Figure 1a, the phase transformation in Cs₂HgBr₄ from incommensurate to

monoclinic phase occurred at $T=233\text{K}$ at cooling is accompanied with a movement of phase boundary. The orientation of the phase boundary, being coincident with the (011) plane. The existence of phase boundary confirms unambiguously the first order of these PTs. The domain structure in Cs₂HgBr₄ crystals appears at $T=233\text{K}$ and exists in the whole temperature range below T_{c1} . Orientation of the domain walls coincides with the planes $Y=0$ and $Z=0$ (Figure 1b,c), as predicted by *Sapriel's* theory for the Fel PT of such a type [5]. No changes in the domain structure have been observed at the PT to triclinic phase ($T_{c2}=167\text{K}$).

The temperature dependences of thermal expansion for the heating and cooling runs are presented in Figure 2. One can see a jump-like elongation of sample occurred only for the b and c principal directions at T_{c1} . Moreover, a small anomalous peak is observed in the vicinity of T_{c1} at heating, which should correspond to absorption of the latent heat at the first-order PT. Only a kink-like peculiarity of thermal expansion indicates a second-order PT into the triclinic phase at T_{c2} . Basing on the data obtained at cooling, we have calculated a temperature dependence of a shear SD component e_4 in the monoclinic phase (see Figure 2, insert). Temperature dependences of optical indicatrix rotation in the adjacent domains are represented in Figure 3.

Table 1.

Sequence of structural phases in Cs₂CdBr₄ and Cs₂HgBr₄ crystals.

| | Cs ₂ CdBr ₄ (see, e.g., [4]) | Cs ₂ HgBr ₄ (see, e.g., [4]) |
|-----------------------------------|--|--|
| Paraelastic phase (mmm) | $T > 252\text{K}$ | $T > 243\text{K}$ |
| Incommensurate phase | $237\text{K} < T < 252\text{K}$ | $230\text{K} < T < 243\text{K}$ |
| Fel phase ($2/m$) | $158\text{K} < T < 237\text{K}$ | $165\text{K} < T < 230\text{K}$ |
| Fel phase ($\bar{1}$), $Z=4$ | $T < 158\text{K}$ | $85\text{K} < T < 165\text{K}$ |
| Fel phase ($\bar{1}$), $Z=8$ | has not been found | $T < 85\text{K}$ |

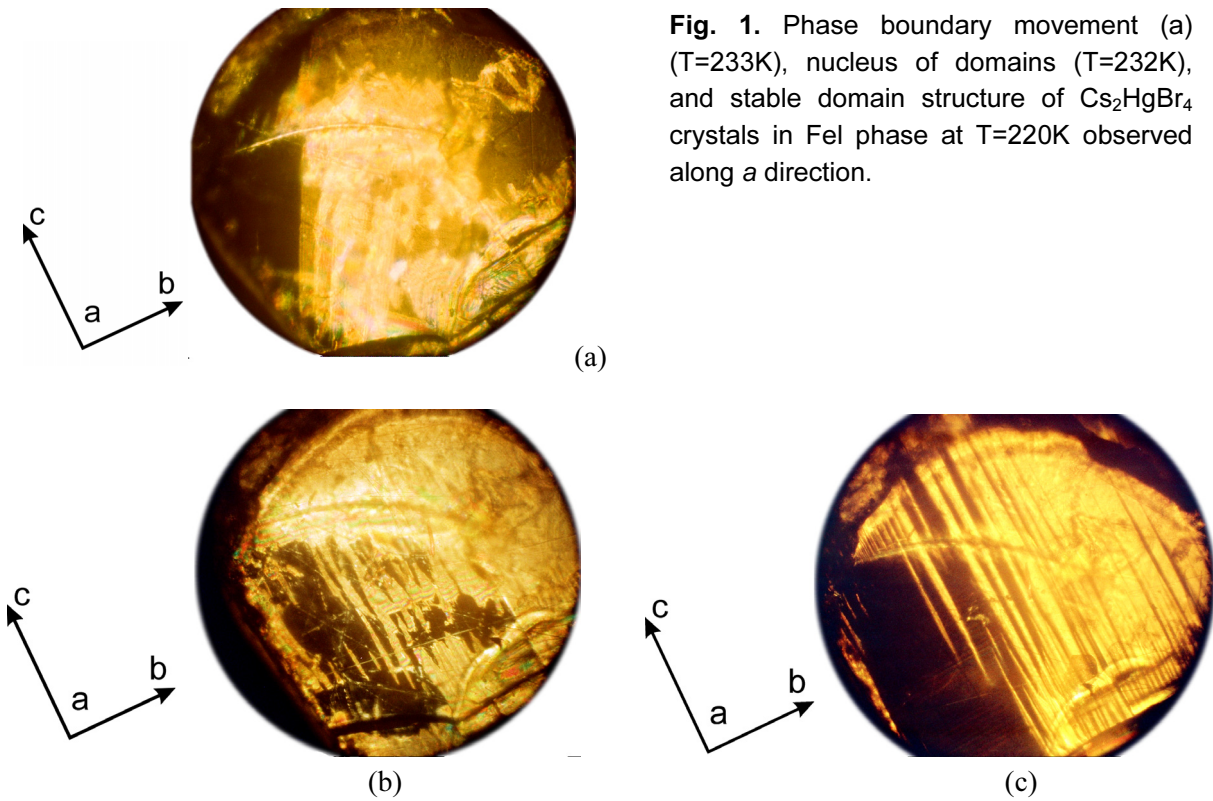


Fig. 1. Phase boundary movement (a) ($T=233\text{K}$), nucleus of domains ($T=232\text{K}$), and stable domain structure of Cs_2HgBr_4 crystals in Fel phase at $T=220\text{K}$ observed along a direction.

b) Cs_2CdBr_4 crystals

Similar results are also obtained for Cs_2CdBr_4 crystals (see Figures 4 and 5). The peculiarities of the experimental data have been only observed at the appearance of phase boundary at $T_{c1}=238\text{K}$. As seen from Figure 4a, the phase boundary possesses two orientations, one of which coinciding with the (011) plane and the other deviating from the $(01\bar{1})$ plane by 12° . Subsequent cooling leads to disappear of the

phase boundaries inclined to $(01\bar{1})$ plane and moving the (011) boundary. Such the behaviour, as well as the existence of mutually non-orthogonal phase boundaries, can evidence a stressed state of the sample, due to temperature gradient or residual stresses.

Using the dependences presented in Figures 3 and 6, the PhEI coefficient p_{44}^c for the paraelastic phase may be calculated with the formula

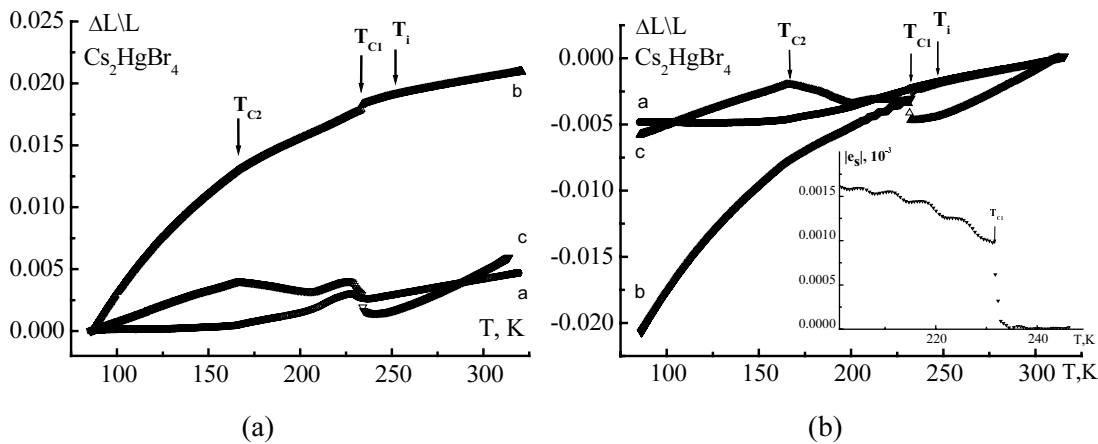


Fig. 2. Temperature dependences of thermal expansions for Cs_2HgBr_4 crystals at heating (a) and cooling (b). T_i corresponds to the commensurate–incommensurate PT. The insert shows temperature dependence of SD in the monoclinic phase.

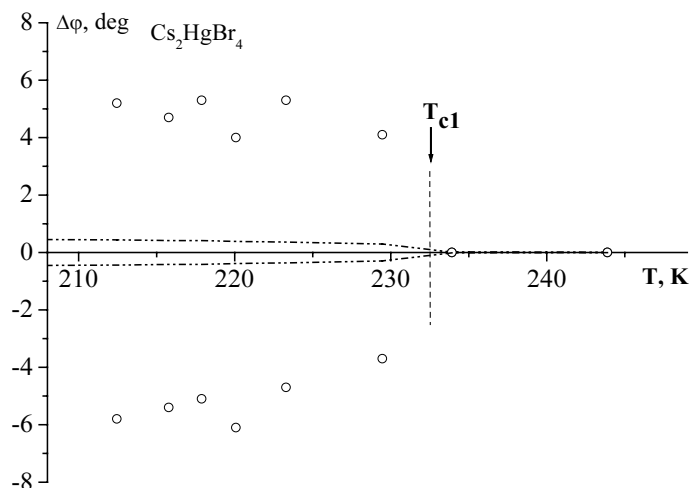


Fig. 3. Temperature dependence of optical indicatrix rotation for the adjacent domains in Cs₂HgBr₄ crystals (circles – the experimental data, dashed line – the calculated contribution of elastooptic effect).

$$p_{44}^c = (B_3 - B_2) \frac{\tan 2\varphi_1}{e_4} \approx \frac{\Delta n_1 \tan 2\varphi_1}{\bar{n} e_4}, \quad (2)$$

where B_3 and B_2 denote the optical-frequency dielectric impermeability coefficients, e_4 the SD, φ_1 the angle of optical indicatrix rotation, Δn_1 the optical birefringence and \bar{n} the mean refractive index. When accounting for that Δn_1 and n are equal to 0.02 and 1.68, respectively,

for Cs₂HgBr₄ and Cs₂CdBr₄ crystals [6], one can obtain the calculated values p_{44}^c of PhEI coefficients for the paraelastic phase. These coefficients are equal to 1.52 and 8.5, respectively. As far as we know, such huge values of PhEI coefficients have not yet been observed in crystals. Thus, we come to conclusion that the rotation of optical indicatrix in the Fel phase is substantially induced by some

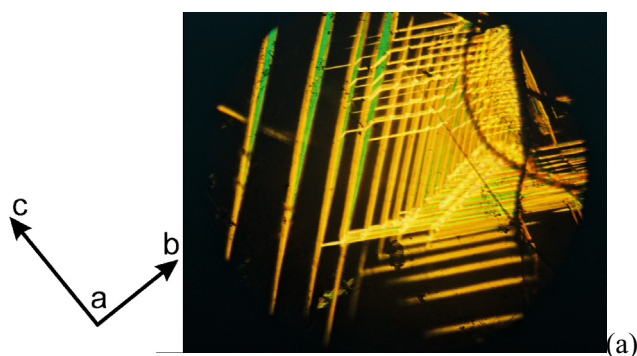
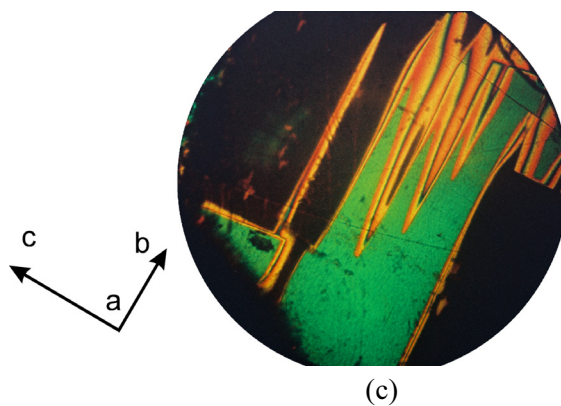
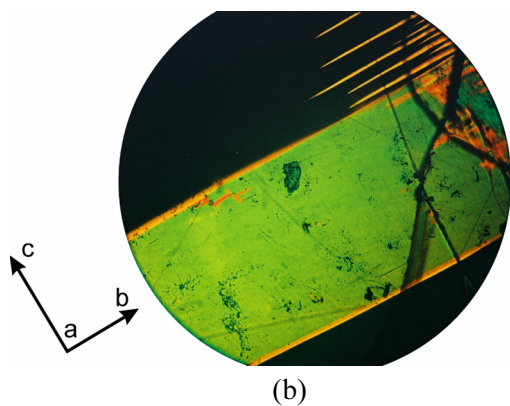


Fig. 4. Heterophase structure in Cs₂CdBr₄ crystals at T=238K (a) and the domain structure in the Fel phase at T=231K (b) and T=208K (c).



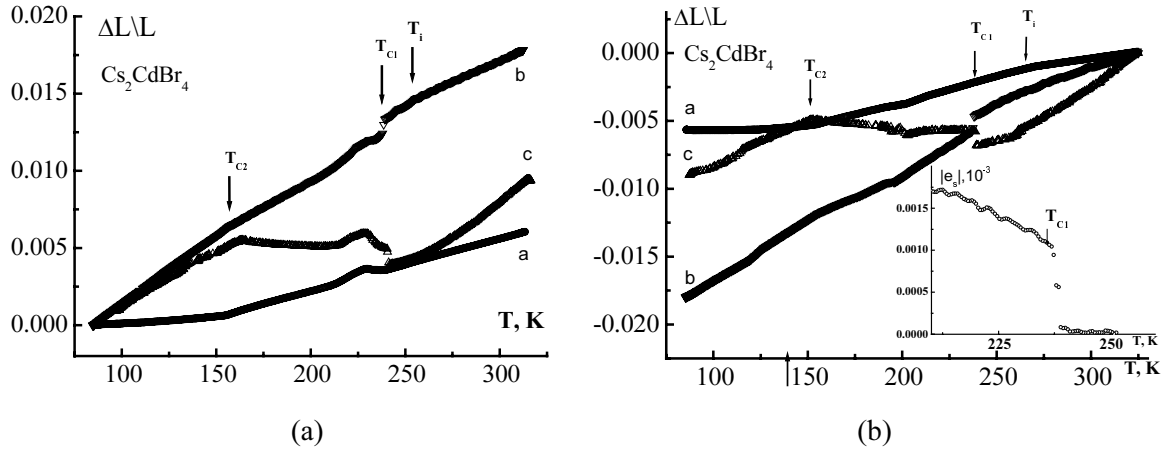


Fig. 5. Temperature dependences of thermal expansion for Cs_2CdBr_4 crystals at heating (a) and cooling (b). T_i corresponds to the commensurate-incommensurate PT. The insert shows temperature dependence of SD in the monoclinic phase.

another order parameter but not the SD and, therefore, the PT in these crystals into the Fel phase looks like improper. Really, let us employ the group-theoretical analysis [7]. Thermodynamic potential written for the centre of Brillouin zone of the normal phase,

$$F = \frac{1}{2}\omega_0^2 Q^2 + \frac{1}{4}BQ^4 + \frac{1}{2}C_{44}^0 e_4^2 + \alpha Q^2 e_4, \quad (3)$$

with ω_0 being the optical soft-mode frequency ($\omega_0^2 = A_0(T_c - T)$) and Q the normal optical phonon coordinate of B_{3g} symmetry, along with the standard minimization procedure

$$\partial F / \partial e_4 = C_{44} e_4 + \alpha Q^2 = 0, \quad (4)$$

result in conclusion that the coupling of SD with the order parameter Q in the Fel phase is nonlinear:

$$e_4 = -\frac{\alpha}{C_{44}} Q^2. \quad (5)$$

The measured values of piezoelectric coefficients of Cs_2HgBr_4 and Cs_2CdBr_4 crystals at the room temperature are $\pi_{44} = 3.85 \times 10^{-11} \text{ m}^2/\text{N}$ and $\pi_{44} = 6.6 \times 10^{-11} \text{ m}^2/\text{N}$, respectively. The PEl coefficients derived on the basis of the known elastic stiffness coefficients (at the room temperature $C_{44} = 3 \times 10^9 \text{ N/m}^2$ for both crystals [3]) are $p_{44}^m = 0.12$ for Cs_2HgBr_4 and $p_{44}^m = 0.2$ for Cs_2CdBr_4 crystals (the superscript “ m ” implies

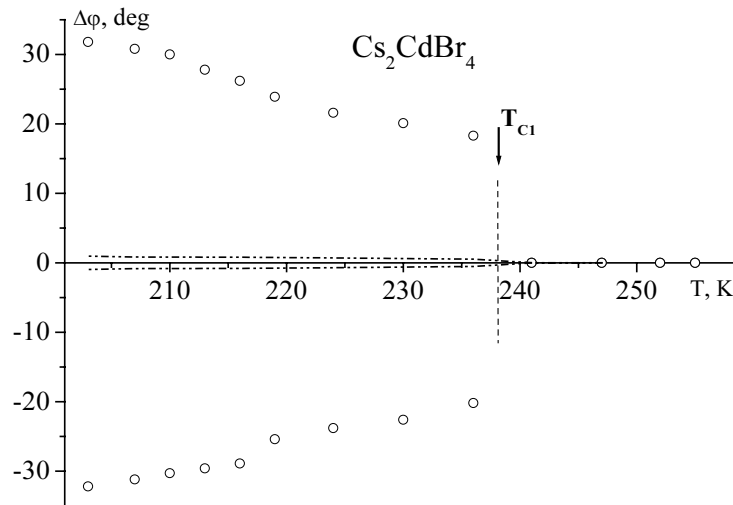


Fig. 6. Temperature dependence of optical indicatrix rotation for the adjacent domains in Cs_2CdBr_4 crystals (circles – the experimental data, dashed line – the calculated contribution of elastooptic effect).

the measured values). There exists significant difference between the values of PhEl coefficients obtained from the optical indicatrix rotation at PT (p_{44}^c) and the direct piezooptic measurements (p_{44}^m). The re-calculated temperature dependences of the optical indicatrix rotation induced by SD in both crystals, based on Eq. (2), are presented in Figures 3 and 6. One can see that the contribution of SD to the optical indicatrix rotation is approximately order of magnitude smaller than that of the order parameter. Hence, the Fel PT in the crystals under studies is improper. One can also estimate their AO FM. The M_2 coefficients amount to the values of $M_2=126.5 \times 10^{-15} \text{ s}^3/\text{kg}$ for Cs₂HgBr₄ and $M_2=366.9 \times 10^{-15} \text{ s}^3/\text{kg}$ for Cs₂CdBr₄ crystals, which are comparable with the characteristics of the best AO materials.

Conclusions

1. It is shown that Cs₂HgBr₄ and Cs₂CdBr₄ crystals are good AO materials. Their PhEl coefficients are respectively $p_{44}=0.12$ and $p_{44}=0.2$, while the AO FM are equal to $M_2=126.5 \times 10^{-15} \text{ s}^3/\text{kg}$ for Cs₂HgBr₄ and $M_2=366.9 \times 10^{-15} \text{ s}^3/\text{kg}$ for Cs₂CdBr₄ crystals.
2. The experimental results testify that the PT to the Fel phase ($2/m$) in both Cs₂HgBr₄ and Cs₂CdBr₄ crystals is a first-order improper one, while the PT into the triclinic phase is of a second order.
3. The orientations of domain walls in the Fel phase and the phase boundary between the incommensurate and Fel phases are determined.

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