Thermal Expansion and Phase Transformation Observation in Cs_2BX_4 (B=Hg, Cd; X=Br, Cl) Crystals

1. Cs_2HgCl_4 crystals

Krupych O., Girnyk I., Trach I., Vlokh R., Vlokh O.

Institute of Physical Optics, 23 Dragomanov Str., 79005, Lviv, Ukraine,
e-mail: vlokh@ifo.lviv.ua

Received: 28.12.2003

Abstract

The results of thermal expansion study and the domain structure observation in Cs_2HgCl_4 crystals are presented. It is shown that the phase transformations in caesium mercury chloride crystals pass through the heterophase regions. The phase transition between the normal and incommensurate (IC) phases is of the first order. The observed “devil's staircase” in the range 143K<T<181K means that the wave vector of the modulated structure has a jump-like temperature dependence, leading to appearance of a complicated sequence of commensurate and IC phases. The non-compatible, inhomogeneous deformations existing in the temperature range 183K<T<225K are, most probably, the reason for appearing the electric polarization. The appearance of ferroelastic domains at 8K below T_{c1} is explained by the existing heterophase structure.

Key words: incommensurate phase, domain structure, thermal expansion.

PACS: 65.70.+y, 77.80.Dj, 78.20.Fm

Introduction

Cs_2BX_4 (B=Hg, Cd; X=Br, Cl) crystals belong to a wide group of crystalline A_2BX_4 compounds [1]. The interest of researches to this family has been stimulated by a presence of incommensurately modulated phases (see, e.g., [2]) in these crystals, as well as the phases with ferroelectric and ferroelastic properties. In Table 1 the temperatures of the phase transitions and the symmetries of the phases occurring in Cs_2BX_4 (B=Hg, Cd; X=Br, Cl) are presented.

The sequences of phase transitions in Cs_2HgBr_4 and Cs_2CdBr_4 are similar and well understood, while the sequence of phase transitions in Cs_2HgCl_4 crystals is essentially different. According to *Kallayev et. al.* [5], these crystals are polar (ferroelectric) in the temperature range 184.5K-196.4K and also below 172.1K. On the other side, the detailed X-ray study of the phase transformations performed by *Bagautdinov and Brown* [4] has revealed at least eight phases. Among those there is a metastable commensurate phase with the space symmetry $Pn2_1a$ or $Pnma$ and the fivefold a parameter, which has been observed only at heating (184K-195K), and a commensurate phase with the space symmetry $P2_12_12_1$ and the sevenfold multiplication of the c parameter, which has been detected in the temperature range 163K-169K. Following from the X-ray analysis, all the commensurate and incommensurate (IC) phases observed below 184K are non-polar, while the existence of spontaneous electric polarization below 172.1K revealed by *Kallayev et. al.* [5] is still incomprehensible. It is important to note that in the temperature ranges where the spontaneous polarization exists, the ferroelectric hysteresis loop has not been ever observed [5]. An interesting behaviour of the domain state has

Table 1.

Phase	**Cs_2CdBr_4** (see, e.g., [3])	**Cs_2HgBr_4** (see, e.g., [3])	**Cs_2HgCl_4**	
			Temperature	Reference
Paraphase (*mmm*)	T>252K	T>243K	T>221K [4]	[4]
IC phase	237K<T<252K	230K<T<243K	184K<T<221K $q=(4/5-\delta)a_o*$	[4]
Ferroelectric phase (*mm2*)	does not exist	does not exist	184K-195K *Pn2₁a* or *Pnma*	[4,5]
Ferroelastic phase (*2/m*)	208K<T<237K	165K<T<230K	175K<T<184K $P112_1/a$, $q=1/3c_o*$ 172K<T<175K $P2_1/n11$, $q=2/5c_o*$	[4]
IC phase	does not exist	does not exist	169K<T<172K $q=(3/7-\delta)c_o*$	[4]
Non-polar phase	does not exist	does not exist	163K<T<169K $P2_12_12_1$, $q=3/7c_o*$	[4]
Ferroelastic phase	does not exist	does not exist	112<T<163K $P12_1/c1$, $q=1/2c_o*$	[4]
Ferroelastic phase ($\bar{1}$), Z=4	T<208K	84K<T<165K	does not exist	
Ferroelastic phase ($\bar{1}$), Z=8	has not been found	T<84K	T<112K, $P1/c1$, $q=1/2c_o*$	[4]

been experimentally found by *Vlokh et. al.* [6] in the commensurate ferroelastic phases (if only one agrees with the conclusions presented in [5]), which happens in the temperature range of 172K<T<184K. Namely, this is the appearance of the domain structure at some intermediate temperature T^*=178K [6] but not at T_c.

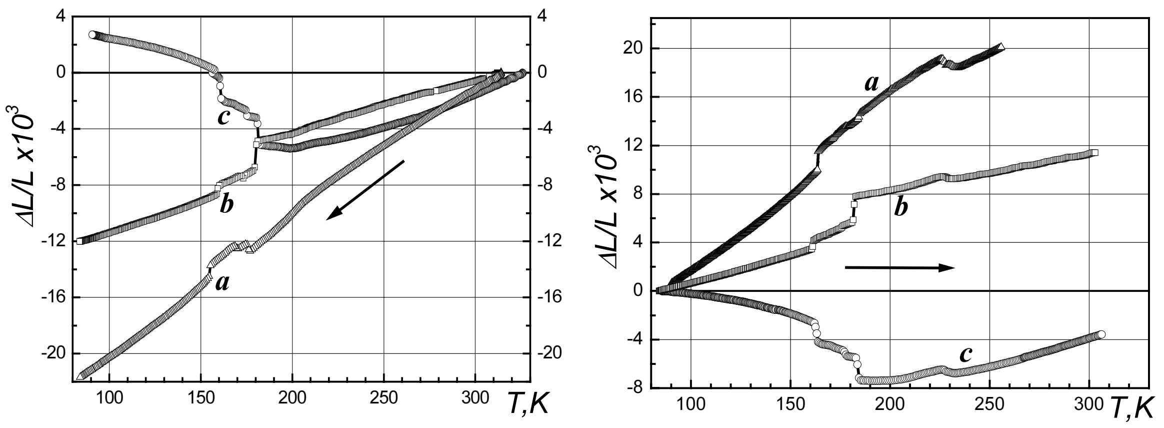
The present paper is devoted to clarifying the mentioned problems, in particular the existence of ferroelectric phase and the reasons for the appearance of domain structure at the intermediate temperature T^*=178K, with the aid of thermal expansion measurements and the optical microscopy methods.

Experimental

Cs_2HgCl_4 crystals were grown by the Bridgman method. The thermal expansion was studied by the capacity dilatometer in cooling and heating temperature runs, with the temperature scan rate $\partial T/\partial t$=1K/min and the sensitivity of 2nm. The observation of the phase transformations was performed with the optical polarization microscope equipped with a cooling cell. The accuracy of determination of the optical indicatrix orientation was ±0.5deg.

Results and discussion

As seen from Figure 1,a, the temperature dependence of thermal expansion in Cs_2HgCl_4 crystals deviates from the linear behaviour peculiar for the normal phase approximately at T_i=239K (in the cooling run). Below this temperature and in the whole range of the IC phase at cooling, we have not observed any appreciable anomalous behaviour of the thermal expansion. Thus, the point T_i=239K may be determined as the temperature of nucleation of the IC phase. However, the maximum referred to the anomalous behaviour of thermal expansion corresponds to T=225K at heating. This maximum, which has been observed only in the heating run, is absent in all the cooling-run dependences. Most probably, it appears due to



a b

Fig. 1. Temperature dependence of thermal expansion in Cs_2HgCl_4 crystals: (a) cooling and (b) heating run.

absorption of the latent heat of the first-order phase transition. One can therefore assume that the phase transition into the IC phase in Cs_2HgCl_4 occurring at T_i represents a diffuse first-order phase transition rather than a second-order one. It is necessary to notice that we have not observed any noticeable anomalous behaviour of thermal expansion at the temperature T=196K, which should correspond to the phase transition into the ferroelectric phase, according to *Kallayev et. al.* [5]. As a consequence, we are predisposed to guess that the ferroelectric phase in Cs_2HgCl_4 crystals does not exist in the temperature range 184K<T<196K.

Moreover, according to *Kallayev et. al.* [5], the ferroelectric hysteresis loop has not been found in the latter range. Besides, the anomalous peak observed by the authors in the dielectric permeability at T=196K is very small (tenth of the ε_b value). Finally, according to the recent X-ray results by *Bagautdinov and Brown* [4], the IC phase in Cs_2HgCl_4 crystals exists in the temperature range 184K<T<221K.

It is evident from Figure 1 that the thermal expansion of Cs_2HgCl_4 exhibits a jump-like anomalous behaviour at T_{c1}=181K (at cooling) and T_{c1}=183K (at heating). The parameter ΔT_h=2K corresponds to the temperature hysteresis of the first-order transition into the ferroelastic phase with the point symmetry group *2/m*. In the course of this phase transition, the crystal undergoes the changes in thermal expansion along the two crystallographic directions *b* and *c*, characterized with the same magnitudes but opposite signs. Such the spontaneous deformation corresponds to the pure shear e_s=e_{32}. The temperature dependence of e_s in the range of ferroelastic phase is presented in Figure 2.

As seen from Figure 2, the spontaneous deformation exhibits at least seven jump-like anomalies at T=181K, 175K, 173K, 166K, 160K, 150K and 143K. The first five points agree more or less with the temperatures reported by *Bagautdinov and Brown* [4]. The temperature behaviour of spontaneous deformation with the step-like changes is an example of the well-known "devil's staircase". A considerable jump of thermal expansion observed by us at T≈160K corresponds, most probably, to the

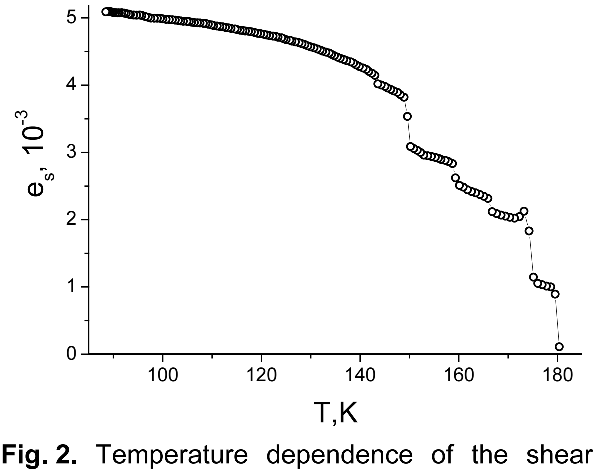


Fig. 2. Temperature dependence of the shear spontaneous deformation in the monoclinic phase.

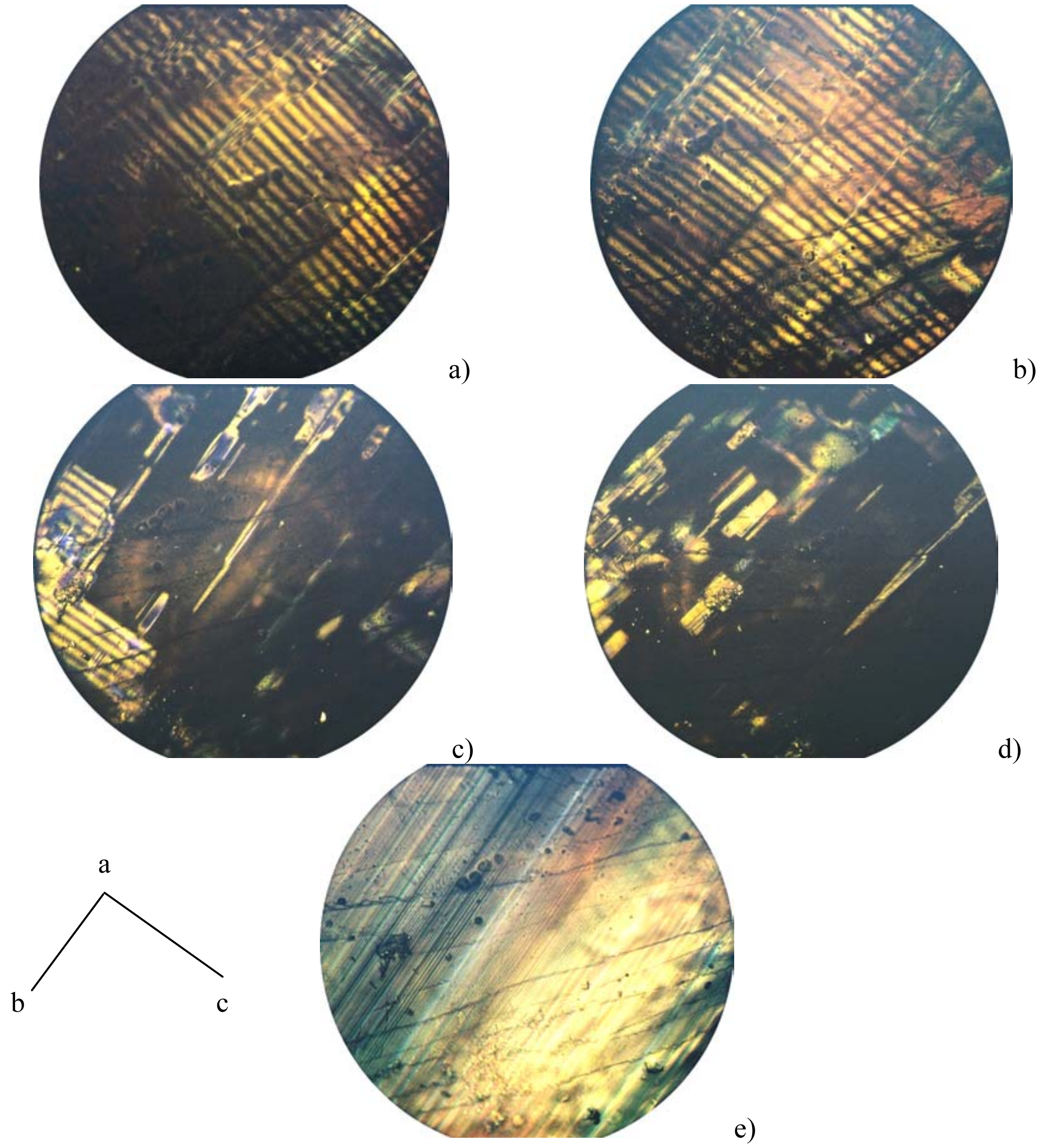


Fig. 3. Movement of phase boundary between the paraelastic and IC phases in Cs_2HgCl_4 crystals along the *b* axis at T=239K (a, b), the heterophase structure in those crystals at T=234K (c) and T=230K (d), and the domain structure in the monoclinic ferroelastic phase at T=162K (e) for d_a=0.4mm.

phase transition into the commensurate ferroelastic phase, which exists down to T=112K and has been defined by *Bagautdinov and Brown* [4] as $P12_1/c1$ ($q = 0.5\, c_o *$). The existence of spontaneous deformation and the “devil’s staircase” in the temperature range of 143K<T<181K proves the fact of phase coexistence in the wide temperature range.

The movement of the phase boundary at T_i=239K (at cooling) is shown in Figure 3. The direction of the phase front movement coincides with the *b* axis. The appearance of the phase boundary between the normal and the IC phases at both cooling and heating confirm unambiguously the above-mentioned assumption that the phase transition at T_i is of the first order. The most interesting feature of this phase boundary is its wave-like shape. The wave consists of dark and bright half-periods. The measured period of the wave is equal to 60μm. The projection of the wave front on [100] plane occupies all the *bc*-square of the sample. The difference in the extinction positions of crystal in the normal and the IC phases, as well as the difference in the extinction positions of the dark and bright half-waves, is 2^o. The former difference is most probably related to "unipolarity" of the modulated IC structure with the wave vector parallel to the *a* axis. The appearance of fringes during the movement of the phase boundary can be explained as a result of its wedge-like movement and misalignment of the optical indicatrices. At further cooling, the heterophase structure that consists of the IC phase and the paraphase, exists down to 221K. The wave-like movement of the phase boundary has been not observed in the sample with the thickness of d_a=0.2mm. This should be predominantly attributed to disappearing the wedge after polishing.

At cooling, the ferroelastic domain structure in Cs_2HgCl_4 crystals has appeared at T=173K, not at T_{c1}=181K. We have not observed the movement of the phase boundary at T_{c1}, probably due to a diffuse character of the phase transition. It is interesting to note that the deformations on the phase boundary taking place at the phase transition $mmm\leftrightarrow 2/m$ are compatible and the lattices of both phases are matched (*Boulesteix at al* [7]). On the other side, it is known (see, e.g., *Roytburd* [8]) that the appearance of the domain structure near the phase boundary with certain concentration of opposite ferroelastic domains, leads to a compensation of non-compatible deformations. Therefore, if the deformations are compatible, as observed in our case, then the appearance of the multi-domain state could cause non-compatible deformations. This fact, along with the phase coexistence in caesium mercury chloride, explains why the sample remains single-domain in the eight-Kelvin region below T_{c1}. The effect of spontaneous switching into the single-domain state observed by us has been earlier mentioned by *Dudnik et. al.* [9]. The ferroelastic domain structure in the monoclinic phase appears at cooling and disappears at heating at T≈173K as a peculiar "photographic development" process. The domain walls are parallel to the *ab* plane. The domain structure is a small-scale one, thus making it impossible to measure the temperature dependence of optical indicatrix rotation in the ferroelastic monoclinic phase.

In the temperature range 183K<T<225K the interference fringes have been observed at heating. These fringes have appeared due to non-compatible deformations between the "mixed" IC phase and the phase that includes spontaneous deformation at the continuous phase transition. Such non-compatible, inhomogeneous deformation can induce electric polarization even in centrosymmetric crystals, owing to a flexo-electric effect. Thus, in our opinion, the polarization observed in [5] does not necessarily means ferroelectricity but has a flexo-electric nature.

Conclusions

Basing on the results reported above, one can conclude that the phase transformations in caesium mercury chloride crystals involve the heterophase regions. The phase transition between the normal phase and the IC phase turns out to be of the first order. The "devil's staircase" observed in the range 143K<T<181K implies that the wave vector of the modulated structure manifests a jump-like temperature behaviour, thus leading to appearance of different phases, of which sequence depends upon a sample prehistory. The non-compatible, inhomogeneous deformations occurring in the temperature range 183K<T<225K are the reason of the electric polarization. Hence, the metastable ferroelectric phase in Cs_2HgCl_4 crystals hardly exist. The appearance of ferroelastic domains in the region of 8K below T_{c1} is explained by the existence of heterophase structure.

Acknowledgement

We wish to acknowledge the financial support from the Ministry of Education and Science of Ukraine under the Project 0103U000703 and Volyn State University (Laboratory of crystal growth) for crystals providing.

References

1. Cummins H. Phys. Rep. **185** (1990) 211.
2. Vlokh O.G., Kityk A.V. Crystalline dielectrics with incommensurately modulated structure. Lviv 2002, 281p.
3. Altermatt D., Arend H., Gramlich V. et al. Acta Cryst. B. **40** (1984) 347.
4. Bagautdinov B., Brown I.D. J. Phys.: Cond. Matt. **12** (2000) 8111.
5. Kallayev S.N., Gladkii V.V., Kirikov V.A., Kamilov I.K. Ferroelectrics. **106** (1990) 299.
6. Vlokh O.G., Gribyk V.G., Kityk A.V. et.al. Cryst. Rep. **35** (1990) 1483.
7. Boulesteix C., Yangui B., Ben Salem M., Manolikas C., Amelinckx S. J. Physique **47** (1986) 461.
8. Roytburd A.L. Phase Trans. **45** (1993) 1.
9. Dudnik E.F., Shuvalov L.A. Ferroelelectics. **98** (1989) 207.