

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

3. The Common Phase Diagram for Cs_2HgCl_4 , Cs_2HgBr_4 and Cs_2CdBr_4 Crystals

Vlokh R., Trach I. and Girnyk I.

Institute of Physical Optics, 23 Dragomanov Str., 79005, L'viv, Ukraine,
e-mail: vlokh@ifp.lviv.ua

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Abstract

On the basis of the literature data and the results of our studies for the heterophase structure, domain structure, phase boundary and Raman scattering the phase diagram common for Cs_2HgCl_4 , Cs_2HgBr_4 and Cs_2CdBr_4 is constructed.

Key words: optical indicatrix, incommensurate structure, domain structure, heterophase structure, phase diagram.

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As mentioned in our previous reports [1,2], Cs_2HgBr_4 and Cs_2CdBr_4 compounds show the same sequence of phase transitions (PTs), while the sequence of structural phases in Cs_2HgCl_4 is essentially different (Figure 1). However, after getting a closer look at those diagrams, one can see that essential differences in the phase

sequence occur only in the temperature range $163 < T < 221\text{K}$ for Cs_2HgCl_4 crystals. Really, the intermediate incommensurate (IC) phase exists in Cs_2HgBr_4 and Cs_2CdBr_4 crystals between the normal and the improper ferroelastic (Fel) phases, whereas in Cs_2HgCl_4 crystals the mentioned intermediate temperature range is

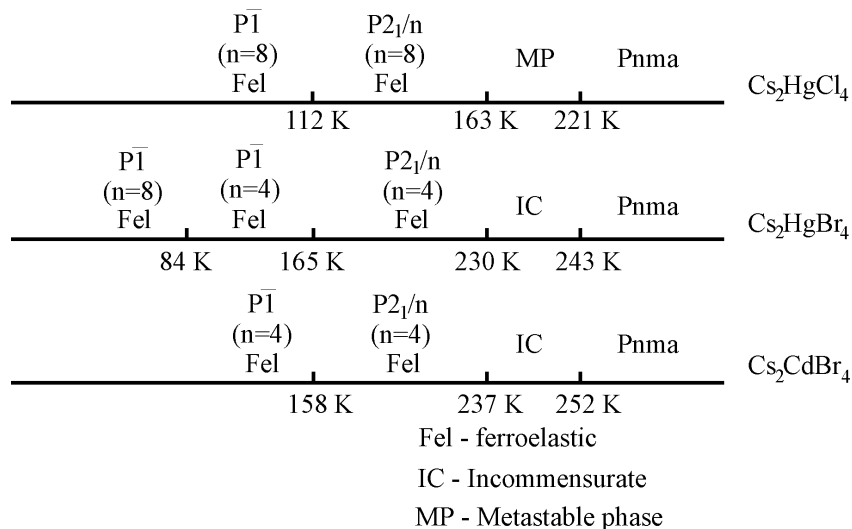


Fig. 1. Sequence of structural phases in Cs_2HgCl_4 , Cs_2HgBr_4 and Cs_2CdBr_4 crystals.

characterized with a number of commensurate and IC phases, whose symmetry groups are subgroups of the normal phase group ($Pnma$, with the four structural units in the elementary cell – $n=4$). The sequence of the intermediate phases and the temperature ranges of their stability differ for different samples, their growth conditions and prehistory.

We shall refer the temperature range of $163 < T < 221$ K in Cs_2HgCl_4 crystals to as the intermediate metastable range. The reasons for correctness of this assumption will be explained below. It is also interesting to recall the behaviour of all three crystals under the hydrostatic pressure [3,4,5]. The P, T -phase diagrams for Cs_2HgBr_4 and Cs_2CdBr_4 are similar: the IC phase disappears under the effect of high hydrostatic pressures. The normal and the IC phases are separated with the lines of second-order PTs and the same holds true for the normal and the Fel phases. At the same time, the IC and the Fel phases are separated with the line of first-order PT. These phase diagrams differ only by the coordinates of the triple point: we have $P, T_T = (100 \text{ MPa}; 259 \text{ K})$ for Cs_2CdBr_4 and $P, T_T = (140 \text{ MPa}; 253 \text{ K})$ for Cs_2HgBr_4 . In case of Cs_2HgCl_4 crystals, the triple point has the coordinates $P, T_T = (140 \text{ MPa}; 220 \text{ K})$. A notable fact is that another triple point takes place in Cs_2HgCl_4 crystals in the vicinity of the atmospheric pressure. Approximately at 10 MPa, the PT from the metastable state to the Fel phase with the symmetry $P2_1/n$ ($q = \frac{1}{2}c_o^*$, $n=8$)

manifests a splitting accompanied with the appearance of improper Fel phase (the symmetry $P2_1/n$, $n=4$). The latter is just the same phase that exists in Cs_2HgBr_4 and Cs_2CdBr_4 crystals below the IC one. Hence, the phase diagrams for all of the mentioned crystals exhibit definitely similar patterns. Considering presumably the P, T -phase diagram for Cs_2HgCl_4 crystals as a common diagram for the three crystals, one can see that the sequence of PTs approximately at 120 MPa corresponds to that of

Cs_2CdBr_4 and Cs_2HgBr_4 (with the only difference that the phase with the symmetry $P\bar{1}$ ($q = \frac{1}{2}c_o^*$, $n=8$) has not been observed in Cs_2CdBr_4 crystals). Thus, there exist all reasons for supposing that the sequence of PTs in the three caesium-containing crystals (Cs_2HgCl_4 , Cs_2HgBr_4 and Cs_2CdBr_4) may be described from the same standpoints, using the constructed common phase diagram. Basing on the analysis of thermodynamic potential, it has been shown in [6] that the normal-to-IC PT in Cs_2CdBr_4 and Cs_2HgBr_4 crystals should be of the second order. Following our previous results [1], the normal-to-metastable PT in Cs_2HgCl_4 crystals is of the first order (*it is accompanied by a movement of phase boundary*). Moreover, the heterophase structures and the internal stresses occur in the samples in the temperature range $163 < T < 221$ K. It is therefore reasonable to assume that, at the atmospheric pressure, there exists a triple point in Cs_2HgCl_4 crystals with the coordinates (0 MPa; 221 K) and the metastable state is peculiar for the temperature interval of $163 < T < 221$ K. The lines of the first-order PTs that separate the normal phase and the improper Fel phase with the symmetry $P2_1/n$ ($q = \frac{1}{2}c_o^*$, $n=8$), as well as the two Fel phases with the symmetries $P2_1/n$ ($q = \frac{1}{2}c_o^*$, $n=8$) and $P2_1/n$ ($n=4$), and the line of the second-order PT that separates the normal and the IC phases converge at this triple point. It is obvious that the line of PTs on the P, T -phase diagram between the Fel phase (the symmetries $P2_1/n$ ($q = \frac{1}{2}c_o^*$, $n=8$) and IC phase in Cs_2HgCl_4 crystals should be vertical in the temperature range $163 < T < 221$ K (Figure 2). This line corresponds to the conditions of atmospheric pressure. As a result, in the temperature range of $163 < T < 221$ K Cs_2HgCl_4 crystals stay on the line of first-order PT at the atmospheric pressure and so thermodynamic conditions are not equilibrium.

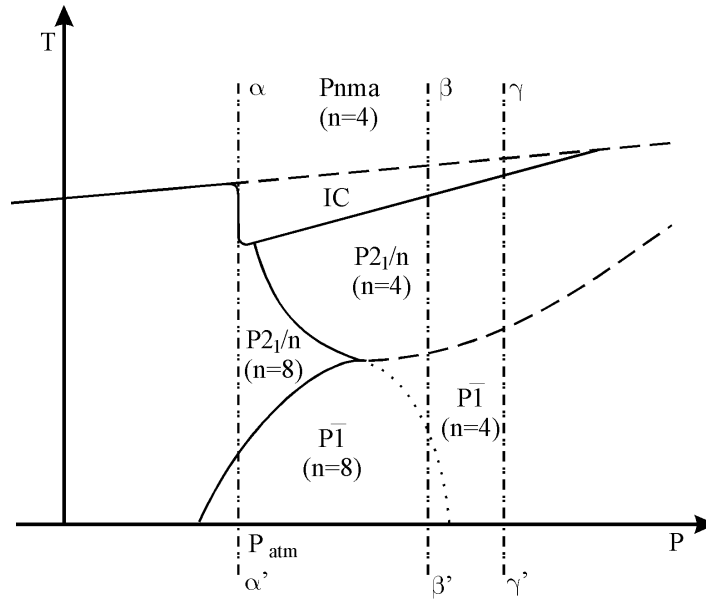


Fig. 2. Schematic P,T-phase diagram for Cs₂HgCl₄ crystals (thermodynamic paths α - α' , β - β' and γ - γ' correspond respectively to the PTs in Cs₂HgCl₄, Cs₂HgBr₄ and Cs₂CdBr₄ crystals at the atmospheric pressure).

Those non-equilibrium conditions are the reason why practically all of the possible structural phases appear inside the small temperature intervals of these metastable states:

the IC phases with $q = \left(\frac{4}{5} - \delta\right)a_o^*$ at

$184\text{K} < T < 221\text{K}$ and $q = \left(\frac{3}{7} - \delta\right)c_o^*$ at

$169\text{K} < T < 172\text{K}$, the Fel phases $P2_1/n$ ($q = \frac{1}{3}c_o^*$) at $175\text{K} < T < 184\text{K}$ and $P2_1/n$

($q = \frac{2}{5}c_o^*$) at $172\text{K} < T < 175\text{K}$, the normal or

ferroelectric phases ($Pn2_1a$ or $Pnma$) at 184K - 195K , and the non-polar phase $P2_12_12_1$

($q = \frac{3}{7}c_o^*$) at $163\text{K} < T < 169\text{K}$ (see the X-ray

analysis presented in [7]). Concerning the low-temperature PTs to the triclinic phase, we have found that the PT between the monoclinic phase $P2_1/n$ ($n=4$) and the triclinic phase $P\bar{1}$ ($n=4$) is of the second order (the phase boundary has not been observed at T_c), while the PT between the monoclinic phase $P2_1/n$ ($n=4$) and the monoclinic phase $P2_1/n$ ($q = 0.5c_o^*$, $n=8$), as

well as the PT between the monoclinic phase $P2_1/n$ ($q = \frac{1}{2}c_o^*$, $n=8$) and the triclinic phase

$P\bar{1}$, ($q = \frac{1}{2}c_o^*$, $n=8$) are the first-order ones

(this fact follows from the jump-like behaviour of ultrasonic waves velocities at T_c [5]). The order of the PT between the triclinic phases with $n=4$ and $n=8$ has not yet been determined. These four lines of PTs could convergent at a ternary point on the phase diagram.

The PTs in Cs₂HgCl₄, Cs₂HgBr₄ and Cs₂CdBr₄ crystals are of the displacement type. This fact has been derived from the Raman scattering studies and the lattice dynamics analysis [8-10]. Displacements of Cs ions lead to softening of the corresponding vibration modes and so result in the PTs. Then the difference in the PT temperatures and a slight difference in the phase sequences should be attributed to influence of crystalline arrangement ($[\text{HgCl}_4]^{2-}$, $[\text{HgBr}_4]^{2-}$ and $[\text{CdBr}_4]^{2-}$ tetrahedrons) on the effective charge of Cs ions. The values of the latter may be obtained from comparison of the phonon frequencies experimentally obtained from the Raman scattering study at room

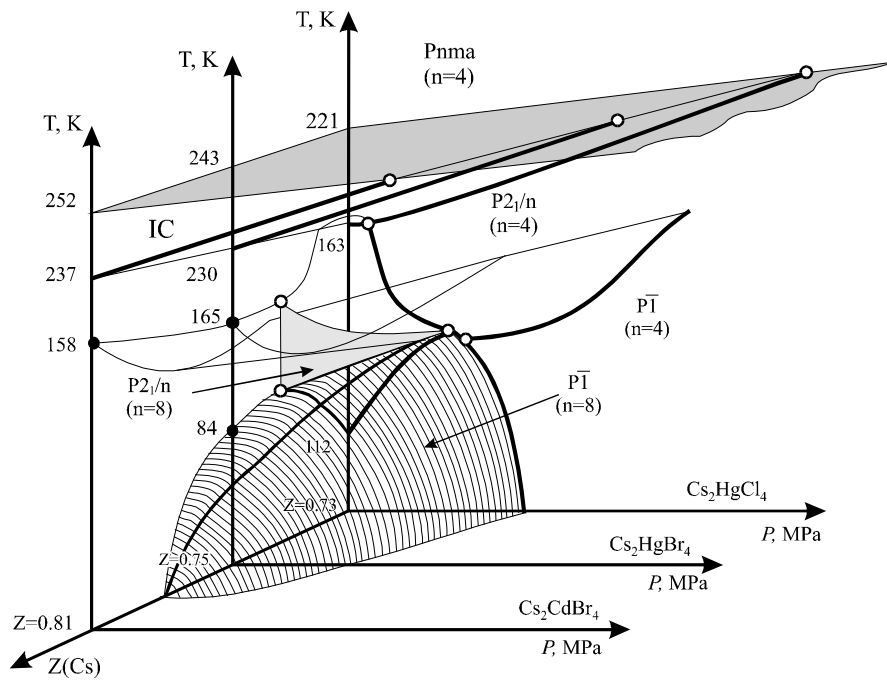


Fig. 3. Phase diagram for Cs_2HgCl_4 , Cs_2HgBr_4 and Cs_2CdBr_4 crystals in terms of the coordinates “effective charge of caesium ions”, hydrostatic pressure and temperature.

temperature [11,12] and the phonon frequencies revealed using the lattice dynamics simulation with the aid of a rigid ion model [13,14]. It has been found that the mean effective charge of Cs ions used as a fitting parameter in frame of those simulations differ for the crystals under consideration. Its value increases from $Z=0.73$ for Cs_2HgCl_4 , through $Z=0.75$ for Cs_2HgBr_4 , up to $Z=0.81$ for Cs_2CdBr_4 crystals.

Thus, one can construct the common phase diagram for all of Cs_2HgCl_4 , Cs_2HgBr_4 and Cs_2CdBr_4 crystals in the coordinates “effective charge of caesium ions”, hydrostatic pressure and temperature (see Figure 3).

Conclusion

On the basis of data taken from the literature and those obtained in the studies of heterophase structure, domain structure, phase boundary, Raman scattering and the lattice dynamics simulations, we have constructed the phase diagram which is common for Cs_2HgCl_4 , Cs_2HgBr_4 and Cs_2CdBr_4 crystals. It is shown that the triple point with the coordinates (0MPa;221K) and the metastable state inside the $163 < T < 221\text{K}$ interval exist in Cs_2HgCl_4 at the

atmospheric pressure. The lines of the four PTs (those among the monoclinic and triclinic phases) on the phase diagram could converge at the ternary point.

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References

1. Krupych O., Girnyk I., Trach I., Vlokh R., Vlokh O. *Ukr. J. Phys. Opt.* **4** (2003) 155.
2. Krupych O., Girnyk I., Trach I., Vlokh R., Vlokh O. *Ukr. J. Phys. Opt.* **5** (2004) 8.
3. Vlokh O., Kityk A., Mokry O. et al. *Soviet Phys.: Solid State* **31** (1989) 312 (in Russian).
4. Vlokh O., Kityk A., Mokry O. et al. *Soviet Phys.: Cryst. Rep.* **35** (1989) 226 (in Russian).
5. Kityk A., Sopronuyk V., Vlokh O. et al. *Soviet Phys.: Solid State* **34** (1992) 2044 (in Russian); Kityk A.V., Shchur Ya.I.,

- Zadorozhna A.V., Trach I.B. et al. Phys.Rev. B **58** (1998) 2505.
6. Vlokh O.G., Kityk A.V. Crystalline dielectrics with incommensurately modulated structure. Lviv 2002, 281p. (in Ukrainian).
 7. Bagautdinov B., Brown I.D. J. Phys.: Cond. Matt. **12** (2000) 8111.
 8. Dmitriev V.P., Yuzyuk Yu.I., Durnev Yu.I., Rabkin L.M., Larin E.S., Pakhomov V.I. Soviet Phys.: Solid State **31** (1989) 91 (in Russian).
 9. Gorban I.S., Korenyuk P.I., Kutovoy S.Yu. Ukr. J. Phys. **35** (1990) 997 (in Ukrainian).
 10. Rodriguez V., Couzi M., Gomez-Cuevas A., Chaminade J.P. Phase Trans. **31** (1991) 75.
 11. Shchur Ya.I., Trach I., Vlokh O. Ukr. J. Phys. Opt. **2** (2001) 192.
 12. Shchur Ya.I., Kityk A.V., Trach I.B., Vlokh O.G. Ukr. J. Phys. **43** (1998) 960.
 13. Chaplot S.L., Rao K.R. and Roy A.P. Phys. Rev. B **29** (1984) 4747.
 14. Chaplot S.L. Rep. BARC-N972, Bhabha Atomic Res. Center, Bombay, 1978.