

Investigation of phase instabilities in guanidinium halogenoplumbates(II)

Marek Szafranski*

Institute of Physics, Adam Mickiewicz University, Umultowska 85, 61-614 Poznań, Poland

Received 26 May 1997; received in revised form 17 October 1997; accepted 21 October 1997

Abstract

Four new compounds based on guanidinium and halogenoplumbate(II) ions, $[\text{C}(\text{NH}_2)_3]_2\text{PbCl}_4$, $[\text{C}(\text{NH}_2)_3]_2\text{PbBr}_4$, $[\text{C}(\text{NH}_2)_3]_2\text{PbI}_4$ and $\text{C}(\text{NH}_2)_3\text{PbI}_3$, have been studied by differential thermal analysis and X-ray powder diffraction. In the chloride, four thermal anomalies have been detected at 345, 383, 412–419 and 439 K, indicating the possibility of four first-order phase transitions; the estimated transition entropies suggest the existence of phase disordering above 439 K. It was established that the phase sequences occurring on heating and on cooling the substance are different. The bromide compound undergoes two successive first-order phase transitions at 406–415 and 426 K, both associated with a large transition entropy indicating disordering of the intermediate- and high-temperature phases. In the tetraiodide, a continuous phase transition to the disordered phase was found at 307 K, while the triiodide undergoes two first-order phase transitions at 255 and 432 K, respectively. Both phase transitions in $\text{C}(\text{NH}_2)_3\text{PbI}_3$ are of the order–disorder type, the high-temperature phase exhibits metastable properties.

The spectroscopic changes observed at the high-temperature phase transitions in $[\text{C}(\text{NH}_2)_3]_2\text{PbBr}_4$ and $\text{C}(\text{NH}_2)_3\text{PbI}_3$ indicate that the mechanism of these transformations is connected both with a disordering process and a distortion of the anionic sublattices. © 1997 Published by Elsevier Science B.V.

Keywords: Disordered structure; Entropy of transition; Guanidinium halogenoplumbates; Phase transition

1. Introduction

Crystals containing complex halogenometallate ions have been widely studied in numerous investigations. Considerable interest has been devoted to compounds of the general formulas AMX_3 and A_2MX_4 , where A is a molecular cation, M a divalent metal and X a halogen. The interest in these substances stems from the variety of phase transitions they undergo (see,

e.g. Refs. [1–9]). Some of them exhibit ferroelectric [8–10] or ferroelastic [4,5,11] properties. The phase transitions in these crystals are often of the order-disorder type, the disordering of the high-temperature phases is most often related to the organic cation [1,2,6,7,9,12]; however, a random distribution between different positions in the crystal lattice of both, cations and anions has also been observed [5]. The structure and properties of AMX_3 and A_2MX_4 crystals depend on the kind of the organic cation, in particular, on its size and shape. A desired modification of certain crystal properties can be reached

*Corresponding author. Fax: 00 48 61 217991; e-mail: masza@phys.amu.edu.pl

through the appropriate choice of organic molecular cation. For example, electronic properties of the layered $(C_nH_{2n+1}NH_3)PbI_4$, perovskite-type semiconductors depend on the length of the alkylammonium chains forming the insulating barriers between semi-conducting PbI_4 layers [13].

In this contribution, the families of AMX_3 and A_2MX_4 crystals are complemented by the compounds containing planar cations: guanidinium halogenoplumbates. In the solid state, the guanidinium cation, $[C(NH_2)_3]^+$, is planar [14] or slightly distorted [15]. Its symmetry is exactly or approximately D_{3h} . Besides, it is a donor of six hydrogen atoms and, thus, can be involved in hydrogen bonds. Recent studies of guanidinium sulfonates [16] and guanidinium nitrate [17] showed that both, the high symmetry of the cation and its ability to form hydrogen bonds are important factors determining the structure and properties of the crystals.

The main objective of our present work was to determine the phase relations in four new compounds based on guanidinium cation and halogenoplumbate(II) anions. We report the results obtained for $[C(NH_2)_3]_2PbCl_4$, $[C(NH_2)_3]_2PbBr_4$, $[C(NH_2)_3]_2PbI_4$ and $C(NH_2)_3PbI_3$.

2. Experimental

The complex compounds obtained in a reaction of AX and MX_2 may crystallize with various stoichiometries [4,10–12] depending on the stoichiometry of the solution, the type of the solvent and the temperature of the solution. It has been observed that two compounds, namely AMX_3 and A_2MX_4 , can be formed even under the same conditions [4].

In the present study the chloride and bromide compounds were synthesized by the addition of a small quantity of a hot aqueous solution of $PbCl_2$ or $PbBr_2$ to a hot aqueous solution of the appropriate guanidinium halide. Needle-like, transparent and colourless crystals were grown by slowly cooling the solutions from ca. 360 K to room temperature. The crystals were identified as $[C(NH_2)_3]_2PbCl_4$ and $[C(NH_2)_3]_2PbBr_4$. The elemental analysis performed using Perkin–Elmer 2400 CHN analyzer and the analysis by atomic absorption spectroscopy gave the

following results:

$[C(NH_2)_3]_2PbCl_4$: C–5.31%(calc. 5.12%),
H–2.61%(2.56%), N–18.72%(17.9%),
Pb–42.81%(44.16%);

$[C(NH_2)_3]_2PbBr_4$: C–3.75%(3.71%),
H–1.93%(1.85%), N–13.27%(12.98%),
Pb–32.83%(32.01%).

The iodides were obtained from a non-stoichiometric aqueous solution of $\frac{1}{4} Pb(CH_3CO_2)_2$ and $C(NH_2)_3I$. Depending on the concentration of the solution, two kind of crystals were grown. They crystallize with different morphology, i.e. as yellow-brown rectangular-shaped plates or yellow needles. These crystals were identified as $[C(NH_2)_3]_2PbI_4$ and $C(NH_2)_3PbI_3$, respectively. The results of the elemental analysis are as follows:

$[C(NH_2)_3]_2PbI_4$: C–2.91%(2.87%),
H–1.52%(1.44%), N–10.22%(10.06%),
Pb–24.20%(24.81%);

$C(NH_2)_3PbI_3$: C–2.02%(1.86%),
H–0.97%(0.93%), N–6.65%(6.48%),
Pb–31.07%(31.96%).

DTA measurements were performed in the 130–500 K temperature range using a home-made apparatus described elsewhere [18]. In the high-temperature region, the measurements were carried out in ambient atmosphere. For the low-temperature measurements, the samples were enclosed in a vacuum chamber ensuring a pressure of 1 Pa, the high-temperature range was limited to 410 K. The masses of the samples were 50–80 mg. The transition enthalpies and entropies were determined on the basis of several DTA curves recorded on heating the sample. Pure indium was used as the reference standard. The accuracy of thus obtained quantities was estimated to be $\pm 20\%$.

X-ray measurements were performed on a DRON 4-07 powder diffractometer with CuK_α radiation. The powder sample was placed in a holder whose temperature was stabilized with an accuracy of ± 0.5 K. The surface of the sample was protected by a thin foil. A thermocouple placed in the sample was used for temperature control.

3. Results and discussion

3.1. $[\text{C}(\text{NH}_2)_3]_2\text{PbCl}_4$

DTA measurements revealed five crystalline phases of $[\text{C}(\text{NH}_2)_3]_2\text{PbCl}_4$, existing in the temperature range between room temperature and the melting point, $T_m=495$ K. Four thermal anomalies were observed every time the sample was heated, the first two of them are shown in Fig. 1. As it has been already established, in the high-temperature region the first heating run is, as a rule, significantly different from the subsequent runs, as is shown in Fig. 2. The differences include an endothermic process appearing only when the crystals are heated for the first time. Presently, it is not clear whether this is a physical process or the crystal decomposition. It is highly interesting that, in the cooling runs, the scheme of the phase transitions differs from that observed on heating. A typical DTA cooling run is represented by curve 4 in Fig. 2. A characteristic feature is that the small anomaly at 412 K precedes a large one at 398 K; thus, the order of the two successive peaks is reversed in the cooling and heating runs. Moreover, sometimes, only a single peak is observed near 412 K instead of two heat anomalies (run 2 in Fig. 2), which indicates that alternative ways for the reverse transformation from the high-temperature phase are possible. All the phase

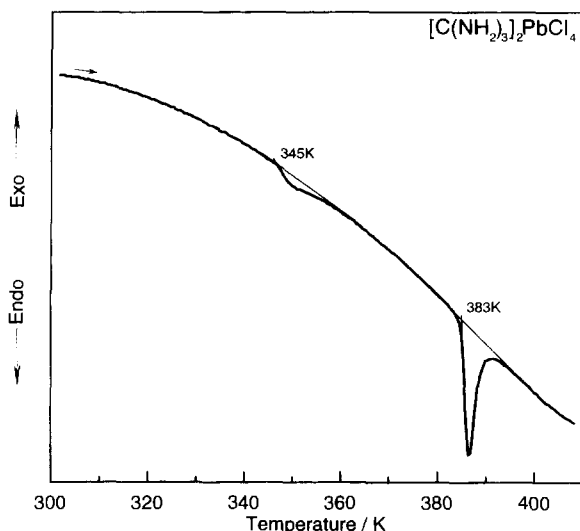


Fig. 1. DTA heating run of $[\text{C}(\text{NH}_2)_3]_2\text{PbCl}_4$ recorded in the 300–410 K temperature range at a rate of 3 K min^{-1} .

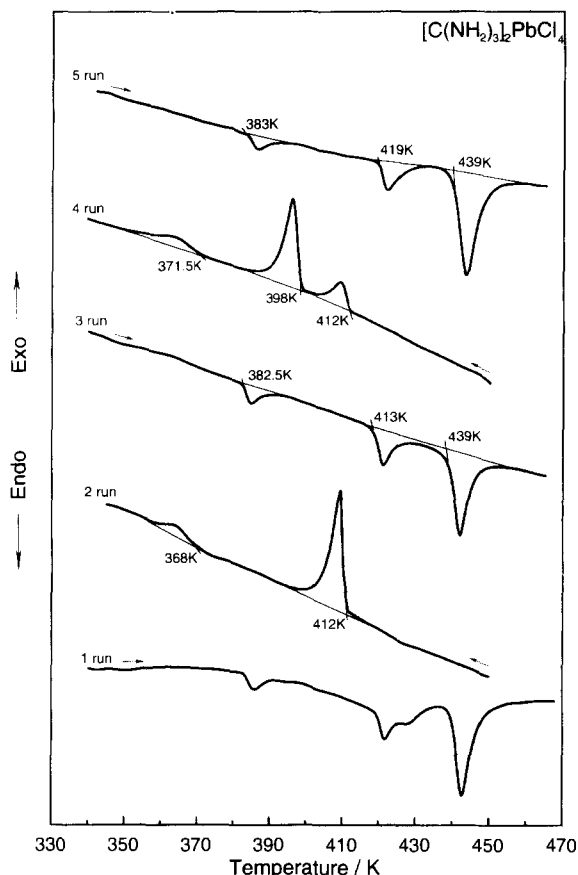


Fig. 2. The high-temperature DTA curves of $[\text{C}(\text{NH}_2)_3]_2\text{PbCl}_4$, the heating/cooling rate was 5 K min^{-1} .

transitions revealed in $[\text{C}(\text{NH}_2)_3]_2\text{PbCl}_4$ are of the first-order, which is suggested by the character of the thermal anomalies and their temperature hysteresis. The enthalpies and entropies of the phase transitions observed in this substance (Table 1) indicate a possible disordering of the phase I existing above 439 K.

The complex picture of the structural transformations in chloride is proved by the X-ray powder diffraction patterns presented in Fig. 3. The phase transitions at 345 and 383 K are hardly observed in the diffraction picture, which reflects a limited extent of the differences between the crystal structures of the phases denoted in Fig. 3 as V, IV and III. More pronounced changes are observed at the III–II and II–I transitions. As can be expected on the basis of the calorimetric results, the phases occurring on cooling

Table 1

Temperatures, enthalpies and entropies of phase transitions in $[\text{C}(\text{NH}_2)_3]_2\text{PbCl}_4$, $[\text{C}(\text{NH}_2)_3]_2\text{PbBr}_4$, $[\text{C}(\text{NH}_2)_3]_2\text{PbI}_4$ and $\text{C}(\text{NH}_2)_3\text{PbI}_3$

Compound	T_i / K	ΔH_i (kJ mol ⁻¹)	ΔS_i (J mol ⁻¹ K ⁻¹)
$[\text{C}(\text{NH}_2)_3]_2\text{PbCl}_4$	345	0.105	0.304 ($R \ln 1.04$)
	383	0.320	0.837 ($R \ln 1.1$)
	412–419	0.877	2.115 ($R \ln 1.3$)
	439	2.567	5.851 ($R \ln 2.0$)
$[\text{C}(\text{NH}_2)_3]_2\text{PbBr}_4$	406–415	8.14	19.92 ($R \ln 11.0$)
	426	7.27	17.06 ($R \ln 7.8$)
$[\text{C}(\text{NH}_2)_3]_2\text{PbI}_4$	307	—	11.3 ($R \ln 3.9$)
$\text{C}(\text{NH}_2)_3\text{PbI}_3$	255	4.476	17.56 ($R \ln 8.3$)
	432	9.85	22.8 ($R \ln 15.5$)

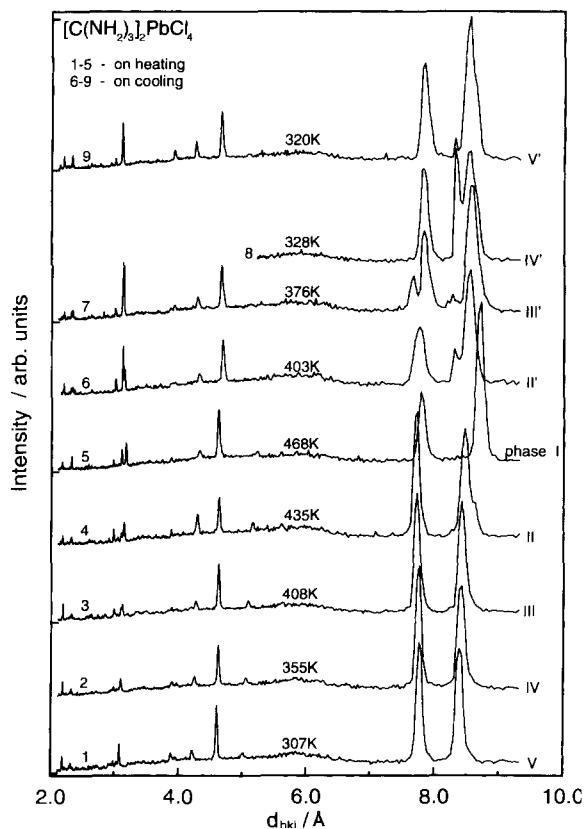


Fig. 3. Powder-diffraction patterns of $[\text{C}(\text{NH}_2)_3]_2\text{PbCl}_4$ at different temperatures. The phases observed on heating and on cooling are denoted by Roman numerals and primed Roman numerals, respectively.

the substance do not have counterparts in the heating cycle. This indicates that the crystals do not transform back to the original room-temperature phase.

3.2. $[\text{C}(\text{NH}_2)_3]_2\text{PbBr}_4$

Fig. 4 shows typical DTA curves recorded for $[\text{C}(\text{NH}_2)_3]_2\text{PbBr}_4$. This substance undergoes two successive phase transitions in the high-temperature region. In the heating runs, the onset of the first

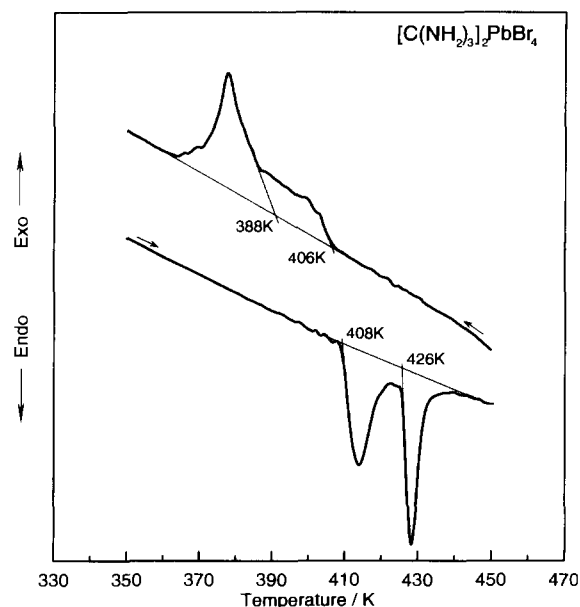


Fig. 4. DTA heating and cooling runs recorded for $[\text{C}(\text{NH}_2)_3]_2\text{PbBr}_4$ at a rate of 2 K min⁻¹.

thermal anomaly occurs in the 406–415 K temperature range (408 K for the heating curve in Fig. 4), the second anomaly is observed near 426 K. The three crystalline phases of $[\text{C}(\text{NH}_2)_3]_2\text{PbBr}_4$ are denoted successively as I, II and III, starting from the phase existing above 426 K. The reverse transformations appear as broad anomalies on the DTA curve at temperatures lower by ca. 20 K. A large hysteresis phenomenon indicates the first-order character of both transitions. It is worth noticing that the colourless crystals take on a yellowish hue when transforming to the high-temperature phase. Upon cooling, they become again colourless but opaque, which suggests pronounced structural changes at the transition temperatures. The rearrangement of the crystal structure is associated with a large transition entropy of III–II as well as II–I transformations (see Table 1). The values of the transition entropies indicate that phase II should be disordered and the transition to phase I is connected with a further rise of disordering in this crystal structure.

3.3. $[\text{C}(\text{NH}_2)_3]_2\text{PbI}_4$

The guanidinium tetraiodide undergoes a phase transition near 307 K. This transition is considered to be of a higher order because of the shape of the thermal anomaly and the lack of any temperature hysteresis phenomenon. As shown in Fig. 5, the transition region is remarkably wide, the precursory effect starts at ca. 260 K and progresses gradually thereafter with increasing temperature. The entropy change associated with the thermal anomaly due to the phase transition is presented graphically in Fig. 5. The estimated overall transition entropy gain is $11.3 \text{ J K}^{-1} \text{ mol}^{-1}$ ($\approx R \ln 4$), which indicates the order-disorder mechanism for this transformation.

3.4. $\text{C}(\text{NH}_2)_3\text{PbI}_3$

The iodide compound crystallizing as a trisalt undergoes two first-order phase transitions. On heating the sample, the first thermal anomaly occurs at 255 K (Fig. 6). The reverse transition usually takes place near 245 K. The value of the transition entropy (Table 1) suggests possible disordering in the phase II.

The experimental DTA curves of $\text{C}(\text{NH}_2)_3\text{PbI}_3$ obtained in the high-temperature region are presented

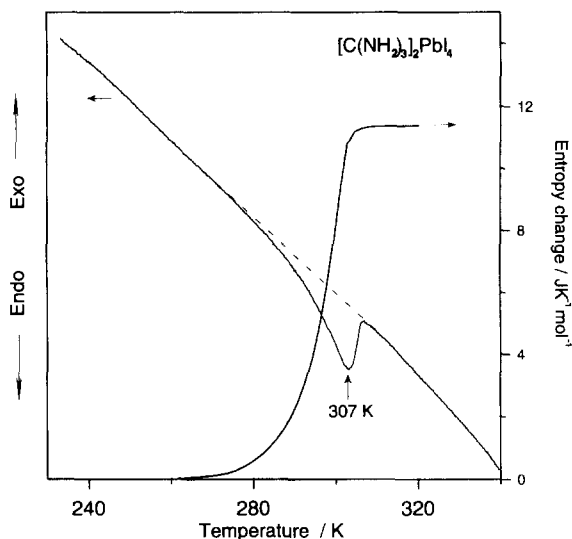


Fig. 5. DTA heating curve (heating rate 3 K min^{-1}) and the temperature dependence of the transition entropy of $[\text{C}(\text{NH}_2)_3]_2\text{PbI}_4$.

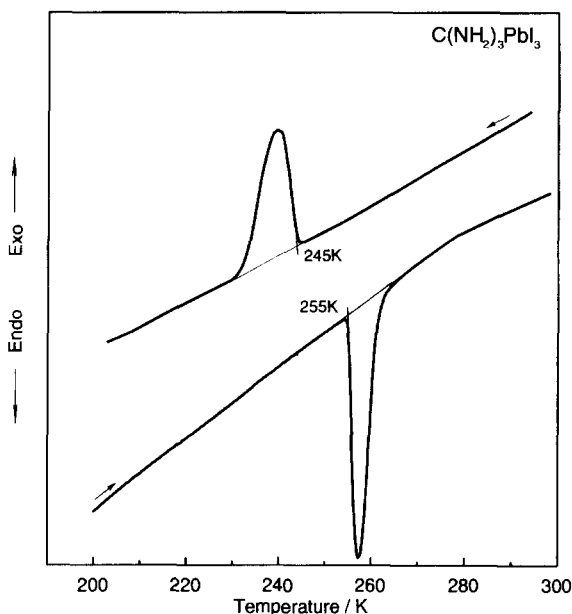


Fig. 6. DTA curves of $\text{C}(\text{NH}_2)_3\text{PbI}_3$ recorded in the low-temperature region, the heating and cooling rate was 2.5 and 3.5 K min^{-1} , respectively.

in Fig. 7. In the first heating run (curve 1 in Fig. 7) the transition from the phase II to the high-temperature phase I was observed near 432 K. The large transition entropy (Table 1) proves that this phase transition is

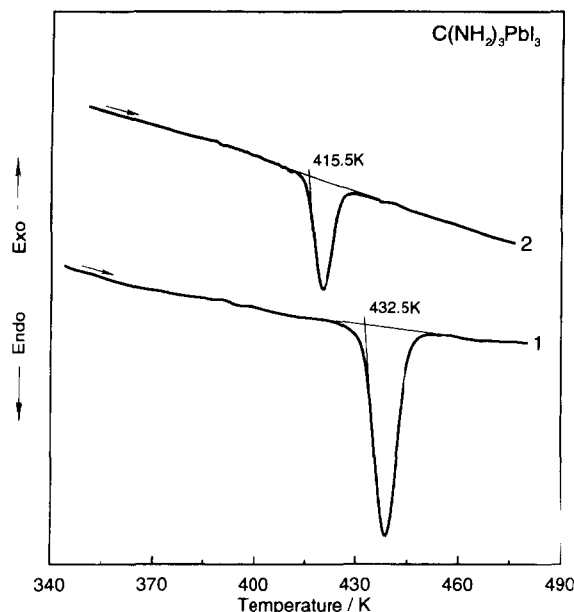


Fig. 7. DTA curves of $C(NH_2)_3PbI_3$ in the high-temperature region, the heating rate was of 5 and 2 $K\ min^{-1}$, respectively, for curve 1 and 2.

also of the order–disorder type. It is interesting that no thermal anomaly was observed on cooling the sample to room temperature, i.e. ca. 140 K below the transition point. It was established that phase I exhibits metastable properties. At ambient pressure and temperature, the crystals transform from this phase to phase II after several hours. As a rule, in the second heating runs the lowering of the transition temperature was observed (compare curves 1 and 2 in Fig. 7). This shift may be explained by the presence of the phase I nuclei which did not fully vanish at room temperature. An interesting feature, also, is a change in the colour of the crystals; when they transform to phase I they become reddish. A gradual restoration of the yellow colour, characteristic for phase II, was observed when the samples previously heated to the phase I temperature were cooled and left at room temperature.

4. Concluding remarks

Each of the three tetrahalides behaves in a different way under the effect of temperature, a continuous phase transition is observed in the tetraiodide while two and four first-order phase transitions occur in the

tetrabromide and tetrachloride, respectively. Hence, it seems that there is no simple relationship between the crystal phases of these substances. An exchange of the halogen atom can modify significantly the anionic sublattice, which, in general, can be formed by isolated ions/aggregates or polyanions connected to infinite low-dimensional structures. It is obvious that the type of the anionic sublattice strongly affects the properties of the crystal.

The spectroscopic changes observed at the high-temperature structural phase transitions in the triiodide and tetrabromide can be a result of the displacements of the halogen atoms forming the Pb^{2+} environment. This indicates that the mechanism of the phase transitions in these crystals is connected not only with an order–disorder phenomenon, but also with a distortion of the anionic sublattice.

Acknowledgements

The author is grateful to Dr. M.A. Kisieliev from JINR, Dubna, Russia, for his assistance with the X-ray powder diffraction measurements.

References

- [1] R.E. Wasylshen, O. Knop, J.B. Macdonald, *Solid State Commun.* 56 (1985) 581.
- [2] A. Poglitsch, D. Weber, *J. Chem. Phys.* 87 (1987) 6373.
- [3] M. Kahrizi, M.O. Steinitz, *Solid State Commun.* 70 (1989) 599.
- [4] P. Vaněk, M. Havránková, F. Smutný, *Solid State Commun.* 77 (1991) 169.
- [5] T. Asahi, K. Hasebe, K. Gesi, *J. Phys. Soc. Jpn.* 61 (1992) 1590.
- [6] R. Blinc, B. Žekš, R. Kind, *Phys. Rev. B* 17 (1978) 3409.
- [7] R. Kind, S. Pleško, H. Arend, R. Blinc, B. Žekš, J. Seliger, B. Ložar, J. Slak, A. Levstic, C. Filipič, V. Žagar, G. Lahajnar, F. Milia, G. Chapuis, *J. Chem. Phys.* 71 (1979) 2118.
- [8] A. Sawada, Y. Shiroishi, A. Yamamoto, M. Takashige, M. Matsuo, *J. Phys. Soc. Jpn.* 44 (1978) 687.
- [9] A.J. Wolthius, W.J. Huiskamp, L.J. De Jongh, R.L. Carlin, *Physica B* 142 (1986) 301.
- [10] E. Fattuzzo, R. Nitsche, H. Roetschi, S. Zingg, *Phys. Rev.* 125 (1961) 514.
- [11] M.C. Valiente, J.I. Marco de Lucas, F. Espeso, Rodriguez, *Solid State Commun.* 86 (1993) 663.
- [12] N. Onoda-Yamamuro, T. Matsuo, H. Suga, *J. Phys. Chem. Solids* 51 (1990) 1383.

- [13] X. Hong, T. Ishihara, A.V. Nurmikko, *Phys. Rev. B* 45 (1992) 6965.
- [14] C.L. Angell, N. Sheppard, A. Yamaguchi, T. Shimanouchi, T. Miyazawa, Mizushima, *Trans. Faraday Soc.* 53 (1957) 589.
- [15] A. Katrusiak, M. Szafrński, *Acta Crystallogr. C* 50 (1994) 1161.
- [16] V.A. Russell, M.C. Etter, M.D. Ward, *J. Amer. Chem. Soc.* 116 (1994) 1941.
- [17] A. Katrusiak, M. Szafrński, *J. Mol. Structure* 378 (1996) 205.
- [18] M. Szafrński, P. Czarnecki, A. Katrusiak, S. Habryło, *Solid State Commun.* 82 (1992) 277.