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Structures of Four New Polytypes of Lead Iodide

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Abstract. Crystals of PbI_2 were grown from a gel at temperatures from 293 to 323 K. Structures of four new polytypes were identified: two hexagonal polytypes belonging to space group $P3m1$: $8H_2$: $(f2f1)_2/(211)_2$ and $30H_1$: $tf2f1(t)_3f2f1(t)_5f2f1/211222211(22)_3112$; and two rhombohedral polytypes belonging to space group $R\bar{3}m$: $24R_1$: $f2of2f4/1(11)_23$ and $36R_1$: $f2(o)_3f2f4/1(11)_43$ (*t–o–f*/Zhdanov notations). Structures of four already known polytypes were recognized: $6H_1$, $12H_1$, $18R_1$ and $18R_2$.

Introduction. The polytypism of PbI_2 discovered by Mitchell (1959) has been investigated extensively in the last two decades: Hanoka & Vand (1968), Agrawal, Chadha & Trigunayat (1970), Prasad & Srivastava (1973), Minagawa (1975, 1979), Chand & Trigunayat (1975*a*,*b*, 1976), Chadha (1976), Chaudhary & Trigunayat (1983). Tens of multilayer polytypes occurring in the crystals obtained from a gel were reported and the structures of 17 were determined completely (these polytypes were listed by Pałosz, 1983). It was established that three polytypes may be considered basic for PbI_2 (Mitchell, 1959): $2H$, $4H$ and $12R$ with Zhdanov sequences 11, 22 and $(13)_3$, respectively (*o*, *t* and $f4f5$ in the *t–o–f* notation, Pałosz, 1980). $2H$ is the low-temperature modification ($2H$ dominates in the crystals grown at room temperature), and $12R$ is the high-temperature structure: only $12R$ is obtained from a vapour phase and this polytype forms from other polytypes, also $2H$, at high temperature (Prasad & Srivastava, 1973; Minagawa, 1975). Based on the experimental data published on the growth and thermal behaviour of the crystals it was concluded by Pałosz (1983) that polytypism of PbI_2 is a function of temperature: the greatest number of polytypes form in the temperature range 320–400 K and the composition of the polytypes changes with temperature. In the present work the effect of temperature on the formation of the polytypes grown from a gel at temperatures between 293 and 323 K is discussed.

Experimental. *Preparation of the crystals.* PbI_2 crystals were grown in silica gel: Mitchell (1959), Henisch (1970), Lefauchaux, Robert, Manghi & Arend (1981). Crystal growth was accomplished in test-tube (single diffusion) and *U*-tube (double diffusion) systems. The best results were obtained in test-tubes 3·0 cm in diameter and 21 cm long. Silica gel was prepared using a 1*M* solution of sodium metasilicate ($Na_2SiO_3.5H_2O$) and acidified to a pH of 4·5 by adding 2*M* acetic acid; Pb^{2+} ions were incorporated into the gel before its setting using 0·5 *M* lead acetate. This solution was poured into the tube and allowed to set at 278 K in a thermostat. After the gel had set (about 4 d) solutions of potassium iodide (concentration varying from 0·1 to 1·0 *M*) were poured into the test-tubes onto the gel. Abundant nucleation was observed after 2 d at the solution–gel interface but crystals started to grow below this interface after 5 d. After a few weeks in darkness, at a temperature thermostatted at 273 to 323 K, many hexagonal and some trigonal plates having diameters up to 5 mm and also some whiskers were grown. A few tens of crystallizations were performed and the structures of 20 to 30 crystals from each crystallization run were examined by X-rays.

X-ray diffraction. The method used here for the identification of PbI_2 polytypes is similar to that used earlier for CdI_2 (Pałosz, 1982), SnS_2 (Pałosz, Pałosz & Gierlotka, 1985) and $SnSe_2$ (Pałosz, Gierlotka & Lévy, 1985). The oscillation photographs were obtained in the 43 mm radius cylindrical camera and with a 0·7 mm collimator. Co $K\alpha$ radiation was used; crystals with the a^* axis as rotation axis were oscillated with the angle between the *c* axis and the incident beam varied between 20 and 35°. In these conditions the reflexions $10.l$ and $1\bar{1}.l$ for which l/N varies between 2·0 and 3·0 were registered on the patterns (*N* is the number of I layers in the cell). The experimental values of the reflexion intensities were measured photometrically. To identify polytypes the reflexion intensities measured experimentally were compared with the values calculated for structural models. The intensities for the reflexions $10.l$ and $1\bar{1}.l$ for the structural models predicted theoretically for the polytypes under investigation have been computed using the expression given by Chand & Trigunayat (1975*a*) and with the f_{Pb}

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Table 1. *Diagram of the xyz coordinates of individual ions of* Pb^{2+} *and* I^- *in polytype cells*

$a_0 = b_0 = 4{\cdot}557$ Å; $c_0 = 3{\cdot}49$ Å; $c = Nc_0$ (N corresponds to N for NH and NR polytypes)

n: position of I layer in the cell; m: position of the molecular layer in the cell

n =	1		2	3		4	5		6
	A	γ	B	C	α	B	A	γ	B
m =		1			2			3	

Layer	x	y	z $n = 2N + 1$	 $n = 2N$
A	0	0	$(n - 1)c_0$	$(n - 0{\cdot}94)c_0$
B	$\frac{2}{3}a_0$	$\frac{1}{3}b_0$	$(n - 1)c_0$	$(n - 0{\cdot}94)c_0$
C	$\frac{1}{3}a_0$	$\frac{2}{3}b_0$	$(n - 1)c_0$	$(n - 0{\cdot}94)c_0$
α	0	0	$(2m - 1{\cdot}47)c_0$	
β	$\frac{2}{3}a_0$	$\frac{1}{3}b_0$	$(2m - 1{\cdot}47)c_0$	
γ	$\frac{1}{3}a_0$	$\frac{2}{3}b_0$	$(2m - 1{\cdot}47)c_0$	

and f_I factors approximated by the analytical function given by Lee & Pakes (1969). The calculated reflexion intensities were corrected for the Lorentz–polarization effect and for spot size. Lattice constants used for calculations and the spatial coordinates of the Pb^{2+} and I^- ions in the polytype cells are given in Table 1. The intensities measured experimentally and those calculated for the polytypes identified are compared in Figs. 1 to 4.*

Discussion. A few hundred PbI_2 crystals grown at different temperatures (293, 308, 323 K) with the use of different concentrations of KI, and also with Ag^+ ions added as impurities, were examined. It was found that independently of growth conditions and impurities the polytype $2H$ dominates in the crystals. In only a few crystals were the basic polytypes $4H$ and $12R$ found. Large-period polytypes were oberved only occasionally, occurring in each case together with $2H$ and frequently also with the basic structure $4H$ and/or $12R$ in coexistence. Five new polytypes were found and structures of four of these were identified completely.

Considering theoretical models for the polytypes under investigation, we used the rules of construction of MX_2 polytypes found earlier for other MX_2 compounds (Pałosz, 1983). To construct probable cells for the polytypes general formulae of the layer stackings were deduced after determination of the symmetry of the experimental patterns, *cf.* division of polytypes into groups (Pałosz, 1980, 1983). The division of PbI_2 polytypes into four groups (and the formulae of the polytype series corresponding to the groups) is similar to that performed for CdI_2 polytypes (Pałosz, 1982). The symmetries of the patterns of CdI_2 and PbI_2 polytypes are also similar, with one exception: the values of the reflexion intensities occurring in the positions $|l/N| = 1, 2, 3, \ldots$ for CdI_2 polytypes of group II are the same for $+l$ and $-l$ reflexions, while these reflexions have different intensities in the case of PbI_2 polytypes. This is because the inter- and intralayer I–I distances are the same for CdI_2, but different (0·43:0·57) for PbI_2. The intensity diagrams used for CdI_2 were prepared for the reflexions in the range of l/N values 2·5–3·5 (1·5–2·5 for SnS_2); the diagrams used for PbI_2 were prepared for the reflexions in the range l/N: 2·0–3·0. We used this range of l/N values for two reasons: we used 15° oscillations and to register the reflexions in the range $\Delta l/N \geq 1$ which are well separated we used Co K and not Cu K radiation; moreover, because of strong absorption of the samples for small-angle reflexions, the reflexions registered in the range $2{\cdot}0 \leq l/N \leq 3{\cdot}0$ are much more suitable for intensity measurement than are those registered in the range $1{\cdot}5 \leq l/N \leq 2{\cdot}5$ (15° oscillations are not enough to register all the reflexions in the range $2{\cdot}5 \leq l/N \leq 3{\cdot}5$). The diagrams used for PbI_2 are different from those used for CdI_2 or SnS_2 but they have symmetries corresponding to each other, this being the basis of division of the polytypes into groups. After determination of the groups to which the polytypes under investigation belong the following models were considered:

$8H$: group I: $(f2f1)_2$

$30H$: group II: This polytype is similar to the polytype $10H$ $(t)_3f2f1$ and only the models having three $f2f1$ sequences were considered: $tf2f1(t)_8(f2f1)_2$, $(t)_9(f2f1)_3$, $(tf2f1)_2(t)_7f2f1$, $tf2f1(t)_2f2f1(t)_6f2f1$, $tf2f1(t)_3f2f1(t)_5f2f1$, $[(t)_2f2f1]_2(t)_5f2f1$, $[(t)_4f2f1]_2tf2f1$, $(t)_2(f2f1)_2(t)_7f2f1$, $(t)_3(f2f1)_2(t)_6f2f1$ and $(t)_4(f2f1)_2(t)_5f2f1$

$24R$: group IV: $f1f5f1o$, $f2of2f4$, $(t)_2f4f5$

$36R$: group IV: $(t)_2f5f1of1$, $(t)_2f4f2of2$, $f5f1(o)_3f1$, $f2(o)_3f2f4$, $(t)_4f4f5$, $(t)_2f4(t)_2f5$, $f2of2f1of1$, $f2(o)_2f2f1f1$, $f2f2f1(o)_2f1$.

The polytypes under investigation were found to be $8H_2$: $(f2f1)_2$; $30H_1$: $tf2f1(t)_3f2f1(t)_5f2f1$; $24R_1$: $f2of2f4$ and $36R_1$: $f2(o)_3f2f4$ as shown in Figs. 1–4 (deposited). Some discrepancies between the values of the measured and calculated reflexion intensities observed in the diagrams occur because some of the polytypes identified occur in syntactic coalescence with basic structures or they contain a certain amount of disorder. Taking into account symmetry of the patterns, the characteristic shapes of the diagrams and the relative values of reflexion intensities, the experimental diagrams agree very well with those calculated.

In the present study no visible effects of temperature in the range 293–323 K, of concentration of the

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* Figs. 1 to 4 and the corresponding tables of observed and calculated intensities have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42248 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

substrates or of the presence of Ag on polytypism of PbI_2 were observed. The multilayer polytypes reported here were usually found occurring in the presence of two basic polytypes $2H$ and $4H$ and/or $12R$. This agrees well with the results reported earlier on other MX_2 compounds where multilayer polytypes were considered as structures intermediate between two different structures (Pałosz, 1983; Pałosz & Przedmojski, 1984): polytypes do not originate from a single structure, they form only when two different basic structures grow simultaneously.

One important fact indicating a difference between isostructural crystals of CdI_2 and PbI_2 should here be stressed. These two materials have similar construction and similar basic structures ($2H$ and $4H$) but in the case of PbI_2 the polytype $12R$ is the third basic structure while this polytype occurs only occasionally in CdI_2. The multilayer polytypes having the stackings $f2$–$f2f4$ occur very rarely in CdI_2 but are frequent in PbI_2: the polytype $18R$: $f2f2f4$ has never been found in CdI_2 but occurs frequently in PbI_2. The above differences between CdI_2 and PbI_2 may be very important in the analysis of the forces governing polytype structure formation.

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Pentasodium Trivanadate Dihydrate

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Abstract. $Na_5V_3O_{10}.2H_2O$, $M_r = 463{\cdot}80$, orthorhombic, $C222_1$, $a = 5{\cdot}9632\,(6)$, $b = 9{\cdot}3751\,(5)$, $c = 20{\cdot}7537\,(8)$ Å, $V = 1160{\cdot}2\,(1)$ Å^3, $Z = 4$, $D_x = 2{\cdot}655$ Mg m^{-3}, Cu $K\alpha_1$, $\lambda = 1{\cdot}540562$, Cu $K\alpha_2$, $\lambda = 1{\cdot}544390$ Å for lattice constants, Mo $K\bar{\alpha}$, $\lambda = 0{\cdot}71073$ Å for intensity measurement, $\mu = 2{\cdot}53$ mm^{-1}, $F(000) = 896$, $T = 298$ K, final $R = 0{\cdot}030$ for 1301 unique observed reflections. The linear chain of the V_3O_{10} group has twofold rotation symmetry and runs parallel to [001]. The V—O—V angle is 122·8 (1)°. The Na^+ ions are situated between the layers of V_3O_{10} groups and are surrounded by six O atoms in an octahedral arrangement.

Introduction. In the course of our studies on alkali-metal vanadates, we tried to prepare single crystals of the low-temperature modification of anhydrous $Na_4V_2O_7$ by evaporating an aqueous solution of $2Na_2O.V_2O_5$ at 373 K, but we obtained two unknown phases instead of the aimed product. One of them was revealed to be $Na_5V_3O_{10}.2H_2O$ by the following structure determination. The structure of the other phase, $Na_4V_2O_7.H_2O$ (tric.), is reported in the following paper (Kato & Takayama-Muromachi, 1985*b*).

While single crystals of $K_5V_3O_{10}$ could be obtained by evaporating aqueous solution and used as specimens for a structure determination (Kato & Takayama-

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