RESEARCH PAPERS

Acta Cryst. (1996). A**52**, 590–595

Growth and Polytype Transformation of AgI-Doped and Undoped PbI_2 Crystals

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(Received 2 October 1995; accepted 15 January 1996)

Abstract

Both undoped and AgI-doped single crystals of lead iodide have been grown by the vapour technique and characterized by X-ray diffraction (XRD) to study their polytype formation. All undoped crystals are exclusively found to contain the stable high-temperature modification, polytype $12R$, while nearly 2/3 of the doped crystals are found to consist additionally of the polytype $4H$ and the room-temperature modification $2H$. The AgI doping is held to be responsible for the formation of $2H$ at the prevalent high temperature of crystal growth. The crystals were subsequently stored for nearly seven months and re-examined through XRD to study possible polytype transformation in them. The undoped crystals did not transform at all but all the doped crystals transformed into the stable room-temperature polytype $2H$. It is concluded that only those crystals that initially have an appreciable number of $2H$ nuclei present eventually transform into the stable $2H$ structure after prolonged storage.

1. Introduction

PbI_2 crystals are isostructural with CdI_2 crystals. However, they show polytypism on a very restricted scale. Nearly 50 PbI_2 polytypes, both hexagonal and rhombohedral have been identified, with complete crystal structures having been found for 21. Unlike CdI_2, the PbI_2 structures are relatively free from one-dimensional disorder. The most stable structure at room temperature is $2H$ and at high temperatures it is $12R$.

PbI_2 single crystals have been grown by the gel, melt and vapour methods. The polytypes have generally been detected in the gel-grown crystals. The vapour-grown crystals usually have the structure $12R$, with the polytype $4H$ sometimes occurring in syntactic coalescence with it.

A systematic study of phase transformation with temperature has been conducted on single crystals of lead iodide grown in gel by various workers. Minagawa (1975, 1981) reported the phase transformation between the room-temperature modification $2H$ and the higher-temperature modification $12R$ and found it reversible. He also reported phase transitions consequent upon prolonged storage of the crystals. Salje, Palosz & Wruck (1987) carried out an exhaustive study of the $2H \rightleftharpoons 12R$ transition through X-ray diffraction and interpreted the results on the basis of the Landau theory of phase transitions. Other results have been reported by Choudhary & Trigunayat (1987) and Mehdi & Trigunayat (1989). The results of all these workers have been tabulated below in *Results and discussion*.

In an extensive study of polytypism of PbI_2 crystals grown by the gel method, Vand & Hanoka (1967) suggested that the presence of silver iodide as an impurity was responsible for the formation of at least some of the PbI_2 polytypes. Subsequently, Mehdi & Trigunayat (1989) observed that the addition of silver iodide in a minute quantity during crystallization appreciably altered the process of phase transformation of the polytypes. It was decided to grow single crystals of both undoped and AgI-doped crystals of lead iodide by the vapour method and study polytype formation by X-ray diffraction. Further, it was planned to store the crystals so investigated for long periods ranging from 6 to 7 months and again explore their polytype behaviour by X-ray diffraction. The results are reported and discussed.

2. Experimental

Analytical grade lead iodide (E. Merk) was purified by the technique of horizontal zone refining. The experimental set-up for purifying the material was similar to that used by earlier workers, *e.g.* Choudhary & Trigunayat (1987), with some modifications to minimize the vibrations in the zone-refining system (Jain & Trigunayat, 1995). The experimental arrangement and the process employed were similar to that used earlier for the growth of single crystals of lead iodide (Jain & Trigunayat, 1995). To obtain the AgI-doped single crystals of PbI_2, PbI_2 and AgI (3% *w*/*w*) were well mixed and put in a small crucible which was placed in the middle portion of a quartz tube in the middle of a cylindrical furnace. The tube was evacuated to a pressure of 1.3–0.13 Pa. The temperature in the middle of the furnace was around 820 K. The crystals grew in about 8–10 h nearly 10 cm away at each end of the tube. The temperature in the region varied from 573 to 593 K. The crystals were found projecting out, perpendicular to the wall of the tube.

For X-ray characterization, oscillation photographs of the crystals were taken about the *a* axis. The oscillation range was chosen so that the angle made by the *c* axis of the crystal with the incident X-ray beam varied between 25 and 40°. This range enables a long sequence of successive 10.*l* reflections to be obtained, which are particularly useful in providing the required structural information. The photographs were recorded on a cylindrical camera of radius 3 cm employing Cu $K\alpha$ radiation. Both the undoped and the doped crystals were stored at room temperature for nearly 6 to 7 months and then again characterized by X-ray diffraction to check for any possible phase transformations.

3. Results and discussion

20 undoped and 20 doped crystals were studied. The results are summarized below:

(*a*) Before storage
    (i) Undoped crystals
        Polytype 12*R* 100%
    (ii) Doped crystals (AgI doping)
        Polytype 12*R* 33%
        Polytype mixture (4*H* + 12*R*) 41%
        (The 12*R* reflections are more intense than the 4*H* reflections.)
    (iii) Polytype mixture (2*H* + 12*R*) 23%
        [The 2*H* reflections are more intense than the 12*R* reflections in most (>70%) of the cases.]
    (iv) Polytype 2*H* 3%
(*b*) After storage
    (i) Undoped crystals
        Polytype 12*R* 100%
    (ii) Doped crystals
        Polytype 2*H* 100%

To interpret the above results, it is useful to recapitulate briefly the available information. Minagawa (1975) reported that when 2*H* samples of lead iodide were annealed at high temperatures (around 420 K), six samples were transformed to faulted 12*R*, coalesced with a small amount of 2*H* and an unidentified component. When some of these samples were stored at room temperature, they converted into 2*H*. These results are summarized in Table 1. Similar results were obtained for more gel-grown crystals (Table 2) (Minagawa, 1981).

Salje *et al.* (1987) reported that, when gel-grown 2*H* samples were annealed from 363 to 403 K, the transformation of the structure began at 366 K and by 403 K 80% of the 2*H* samples were transformed to 12*R*. Also, the crystals heated above 425 K were completely transformed to 12*R*. When the samples were stored at room temperature, only the samples that had some 2*H* in them before storage eventually converted into 2*H*. These results are presented in Table 3.

Choudhary & Trigunayat (1987) observed that their melt-grown crystals of intermediate purity reverted to the 2*H* structure upon storage for nearly nine months. The polytype 2*H* was present in them before storage. The very impure and very pure crystals did not have 2*H* in them and did not revert to 2*H* upon storage (Table 4).

Mehdi & Trigunayat (1989) found that those gel-grown PbI_2 crystals that mainly consisted of 2*H* transformed to 12*R* when heated around 420 K. But higher (4*H*, 12*H*, 16*H*) and unidentified polytypes did not transform into 12*R*. On prolonged storage at room temperature, all the heat-treated crystals were restored to the original 2*H*. However, such storage had no effect on the structures of higher and unidentified polytypes, whether present singly or in combination with 12*R* (Table 5).

Inomata, Inoue & Kijima (1968) studied polytype transformation resulting from heating single crystals of SiC at high temperatures (up to nearly 2570 K). They concluded that the crystal structure of a polytype 2*H*, believed to be the stable room-temperature modification of SiC, did not transform into the high-temperature modification 6*H* unless the original structure 2*H* had some 6*H* nuclei present in it.

A thorough X-ray diffraction study of the transformation 3*C* → 2*H* resulting from heat treatment of single ZnS crystals was carried out by Frey, Jagodzinski & Steger (1986). The cubic 3*C* and the hexagonal 2*H* are two distinct stable phases of ZnS. The 3*C* phase is known to be the low-temperature configuration, whereas the 2*H* phase is believed to have its stability range at higher temperatures (> 1270 K). When single crystals of the 3*C* phase were annealed above 1290 K, various polytypes were formed as intermediate phases. Each crystal revealed its own characteristic transformation behaviour depending on the amount of disorder and had its own transformation point. Almost defect-free crystals showed no transformation. The transformation behaviour was not found to be uniform throughout a sample but depended strongly on the amount of defect and possibly also on their kind. It followed that the transformation 3*C* → 2*H* required the existence of disordered regions in the original 3*C* phase, which helped in the growth of 2*H* nuclei at an appropriate temperature, finally resulting in the transformation of the crystal into the 2*H* phase.

Empirically, the polytypes 2*H* and 12*R* are believed to be the thermodynamically stable room-temperature modification and high-temperature modification, respectively, of lead iodide. From the aforementioned results of the large number of investigations of polytype transformation, it may be concluded that only those crystals that have an appreciable number of 2*H* nuclei

Table 1. *Minagawa's (1975) results of X-ray characterization of both gel-grown and vapour-grown crystals*

Anealing

No. of crystals	Starting material/structure	Sub-category	Heating temp. (K)	Heating time (h)	Resulting structure	Remarks
Gel grown (8)						
6	2*H*	(1)	420	120 (5 d)	Faulted 12*R* + weak 2*H* + un	A typical photograph shown
2	2*H*	(2)	420	120	4*H*	The resulting 4*H* was further annealed
	4*H*		570	24 (1 d)	12*R*	
Vapour grown (4)						
	Powder		670 K (growth temp.)			
3		(1)		-	Ordered 12*R* (obverse + reverse) one with small amount of 4*H*	
1		(2)		-	Ordered 12*R*	

Storage

No. of crystals	Starting structure	Sub-category	Duration of storage (months)	Resulting structure	Remarks
Gel grown (8)					
4	Faulted 12*R* + weak 2*H* + un	(1)	1	2*H* + faulted weak 12*R* + un	A typical photograph shown
2	Faulted 12*R* + weak 2*H* + un	(1)	2	Faulted 12*R* + weak 2*H* + un	(Do not transform to 2*H*)
2	12*R*	(2)	-	-	Effect of storage not mentioned
Vapour grown (4)					
3	Ordered 12*R* (one with weak 4*H*)	(1)	1.5	2*H*	Even 4*H* → 2*H*
1	Ordered 12*R*	(2)	2	No change	

present in them eventually transform into the stable 2*H* structure after prolonged storage at room temperature. Thus, the existence of 2*H* nuclei in the primary structure appears to act as a 'catalyst' for bringing about a complete (or nearly complete) transformation of the structure to 2*H*. The presence of 2*H* nuclei should usually manifest itself on an X-ray photograph as discrete diffraction spots, albeit of low intensity, but sometimes if their proportion is comparatively very small they remain undetected. This has to be borne in mind when drawing inferences from the said investigations. *Prima facie*, Minagawa's result (Table 1) on the storage of two gel-grown crystals, consisting of a mixture (faulted 12*R* + weak 2*H* + unidentified type), appears to contradict the general conclusion that the crystals having 2*H* as a component in their structure finally transform into the 2*H* structure. However, it is noted here that, besides some 2*H*, the primary structure mainly consists of a disordered 12*R* polytype, along with some unidentified polytype, whose existence is also believed to be associated with the presence of some kind of disorder in the structure. The disorder is mainly believed to consist of dislocations and stacking faults. If the degree or disorder in the primary structure is relatively high, it will act as a strong deterrent to the expansion of the 2*H* nuclei in the structure, thus preventing the transformation of the structure into the stable room-temperature phase 2*H*. The phase transition from one polytype structure to another essentially necessitates a rearrangement of the atomic layers in the initial structure, which can occur smoothly only when the structure has little or no disorder. As the disorder increases, the rearrangement will become increasingly difficult, so much so that for an exceedingly high structural disorder it will be rendered almost impossible. It may be noted in Minagawa's results (Table 1) that four more gel-grown crystals with the same initial structure (faulted 12*R* + weak 2*H* + un) succeeded in transforming to the 2*H* structure (in coalescence with a weak faulted 12*R* and an unidentified type). Although the degree of disorder of his faulted 12*R* crystals was not reported by Minagawa, either qualitatively or quantitatively, it may be safely assumed that the two crystals with faulted 12*R* structures that did not transform into 2*H* upon storage at room temperature were comparatively much more disordered than the other set of four faulted crystals that nearly transformed into 2*H* after storage.

Table 2. *More results of X-ray characterization of gel-grown crystals (Minagawa, 1981)*

Annealing

No. of crystals	Heating temp. (K)	Heating time	Starting structure	Resulting structure	Remarks
Gel grown (9)					
1	450	2–3 min	2*H*	Faulted 12*R*	Quenched to room temp. after heating
2	(*a*) 450	2–3 min	2*H*	Faulted 12*R* + weak 2*H*	Quenched to room temp. each time
	(*b*) 470			Faulted 12*R*′ + weaker 2*H* (less disordered)	
	(*c*) 530			Still less disordered 12*R* + still weaker 2*H*	
	(*d*) 570			12*R*	
3, 4	570	24 h	2*H*	Faulted 12*R* + weak 2*H*	Quenched to room temp. each time
5–9	570	24 h	2*H*	Faulted 12*R* + weak 2*H*	Quenched to room temp. each time

Storage

No. of crystals	Starting structure	Duration of storage	Resulting structure	Remarks
5 to 9	Faulted 12*R* + weak 2*H*	1–3 months	Weak faulted 12*R* + intense 2*H*	Effect of storage on crystals 1–4 is not mentioned

Minagawa's work involves both gel-grown and vapour-grown crystals. In comparison to gel growth, in which impurities may enter the crystals from both the reactants and the gel medium, vapour growth is expected to yield far purer crystals as it involves just one component from which only the volatile impurities can get into the crystals The local lattice strains at the positions of the impurities produce dislocations and stacking faults. Consequently, the gel-grown crystals are prone to be strongly disordered compared with the vapour-grown crystals. This is clearly manifested in Minagawa's results (Tables 1 and 2), in which the gel-grown crystals are generally found to be faulted but the vapour-grown crystals are all ordered. Further, in the results of storage of the vapour-grown crystals, it should be noted that three out of the four crystals transformed into the room-temperature modification 2*H*, presumably because they initially contained 2*H* nuclei, which could bring about the necessary rearrangement of the layers in the absence of disorder in the crystals. The structure of the fourth crystal remaining intact after the storage implies that initially it did not contain any 2*H* nuclei. This also shows that mere thermodynamical requirements are not sufficient to drive a structure towards another structure of greater thermodynamic stability; initial presence of the 2*H* nuclei in the structure is a necessity.

With these results in view, the effect of storage on the AgI-doped single crystals of lead iodide can be analysed. In about 1/4 of these crystals, the polytype 2*H* is found to be present, either singly or in coalescence with 12*R*. In the rest of the cases, the polytype 12*R* is found to be present singly or in coalescence with 4*H*. The formation of 12*R* in nearly 3/4 of the cases, either singly or in coalescence with 4*H*, is expected on the basis of the known pronounced thermodynamical stability of the 12*R* PbI_2 polytype at high temperatures. Further, the intensity of the 12*R* reflections is expected to be higher than the intensity of the 4*H* reflections as follows. The 4*H* structure is generally known to be formed during phase transformation from the stable low-temperature modification 2*H* to the stable high-temperature modification 12*R* on heat treatment, as reported by several workers, *e.g.* Palosz (1983). However, its temperature range of stability has not been specified. According to Palosz (1983), it forms within the temperature range of ~420 K to nearly the melting point of PbI_2, *viz* 675 K. Thus, the formation of 4*H* is expected in the temperature region of crystal growth employed by us, *viz* 570–590 K; this is experimentally well supported by its observed occurrence in 40% of cases in the present work. However, because of the dominant thermodynamic stability of 12*R* at high temperatures, which causes all PbI_2 polytypes to ultimately convert into 12*R* on heat treatment (Minagawa, 1981), it is naturally expected that in the crystals containing the polytype mixture (4*H* + 12*R*) the proportion of 12*R* will be higher, resulting in more intense 12*R* reflections on the X-ray photographs in comparison with the 4*H* reflections. In the rest of the cases, constituting nearly 1/4 of the total, the structures (2*H* + 12*R*) or 2*H* have been formed. The polytype 2*H* is regarded as the room-temperature stable modification of lead iodide. Normally, it cannot be expected to form at the high temperature of crystal growth employed in the present work, *viz* around 570 K. Its formation has to be attributed to the AgI doping, as follows. The cell dimensions of PbI_2 ($a = b = 4.60$, $c = 6.98$ Å) and AgI

Table 3. *Salje et al.'s (1987) results of X-ray characterization of gel-grown crystals*

Annealing

Category	Starting structure	Heating temp. (K)	Heating time (h)	Resulting structure	Remarks
(i)	2*H*	340	12	–	
		345		2*H*	Diffraction pattern taken every 12 h of heating. After 5 d, temp. increased by 5 K. This was continued until the crystal transformed to 12*R*. The amount of transformed material was estimated from the relative intensities of 12*R* and basic 2*H* after each experiment. No transformation up to 365 K
		⋮			
		365		2*H*	
(ii)	2*H*	(*a*) 366	7		Phase transformation almost complete for annealing time of 100 h. For 369, 372 and 378 K, a graph was drawn of (annealing time) *vs* $(1/T) \times 10^3\,K^{-1}$, showing decrease in annealing time with increase in temp.
		(*b*) 369		2*H* + 12*R* (Transformation just begins)	
		(*c*) 372			
		(*d*) 375			
		(*e*) 378			
		(*f*) 383			
		(*g*) 400			90% of material 2*H* → 12*R*
(iii)	2*H*	Above 425 K	Not mentioned	12*R*	All transformed completely into 12*R* after long annealing (annealing time not mentioned)

Storage

Category	Starting structure	Duration of storage	Resulting structure	Remarks
(i)	2*H*	–	Not mentioned	The structure 2*H* itself is the stable room-temperature modification of lead iodide
(ii)	12*R* + 2*H*	2–10 weeks	2*H*	On annealing, 90% 2*H* → 12*R*, which implies that 2*H* was also present before storage. No correlation was observed between the thermal history of the sample and the rate of back transformation, in agreement with Minagawa (1981)
(iii)	12*R*	16 weeks	12*R*	Remained 12*R*

Table 4. *Choudhary & Trigunayat's (1987) results of X-ray characterization of melt-grown crystals*

Storage (samples of different purities)

Category	Purity (No. of zone passes)	Starting structure	Duration of storage	Resulting structure	Remarks
(i)	Less pure (6–8 zone passes)	68%: $12R_o/12R_R/(12R_o + 12R_R)$	12 months	No change	
		32%: $(4H + 12R)$			
(ii)	More pure (12–14 zone passes) (Intermediate purity)	78%: $12R_o/12R_R/(12R_o + 12R_R)$	9 months	2*H*	All but one crystal transformed to 2*H*
		18%: $(4H + 12R)$			
		8%: $(2H + 12R)$			
(iii)	Very pure (20 zone passes)	100%: $12R_o/12R_R$	7 months	No change	

($a = b = 4.58$, $c = 7.49$ Å) are similar, particularly in the *ab* planes. The AgI 2*H* polytype has been reported to form in a wide range of temperatures, *viz* room temperature to ~820 K (Prager, 1974). Although the proportion of AgI in the basic material is small, *viz* 3%, nevertheless microcrystals of AgI-2*H* can form during growth. The near-perfect lattice matching in the *ab* plane, which constitutes the basal surfaces on which the nucleation takes place during crystal growth, will strongly favour epitaxic growth of PbI_2-2*H* structure around them. If an AgI-2*H* nucleus forms in the early stages of crystal growth, the resulting final structure will be PbI_2-2*H*, without admixture of 12*R*. This has been observed to happen in one case. However, on account of the preponderant proportion of PbI_2 in the basic material (97%) and the dominant stability of PbI_2-12*R* in the temperature range of crystal growth (570–590 K), formation of the AgI-2*H* nuclei is likely to be

Table 5. *Mehdi & Trigunayat's (1989) results of X-ray characterization of gel-grown crystals*

Crystals	As-grown	After initial heating (~10 h)	After final heatings (~50 h)
Undoped (20) (No. of X-ray photographs for as-grown crystals: 40)	All type 2*H* No streaking (except one case of light streaking) No arcing	All type 4*H* Light streaking: 34 Medium streaking: 4 Light arcing: 21 Medium arcing: 3	Either $12R_R$ or $12R_o$ Light streaking: 23 Medium streaking: 14 Heavy streaking: 3 Light arcing: 18 Medium arcing: 9 Heavy arcing: 3
AgI doped (15) (No. of X-ray photographs for as-grown crystals: 30)	2*H* (21); 4*H* (3); 12*H* (2); 16*H* (1); 12*R* (3) Light streaking in 9 cases (2*H* : 3; 4*H* : 3; 12*R* : 1; 12*H*: 1; 16*H*: 1) Light arcing in two cases (both 12*R*)	2*H* → 4*H* (16), 2*H* → (4*H* + un)* (2), 2*H* → (4*H* + 12*R* + un) (1), 2*H* → (2*H* + un) (2) No change in the rest Light streaking in all cases, except two cases of 2*H* and three cases of 12*R* Light arcing in eight cases (2*H*: 2; 4*H*: 3; 12*R*: 3); medium arcing in two cases (12*H*: 1; 16*H* : 1)	2*H* → ($12R_R + 12R_o + 4H$) (16) 2*H* → ($12R_R + 12R_o$ + un) (4), 2*H* → (12*R* + 4*H* + un) (1) All 4*H* changed to ($4H + 12R_R + 12R_o$) No changes in 12*H* and 16*H* Light streaking: 21 (12*H*: 14; 4*H*: 2; 12*R*: 3; 12*H*: 1; 16*H*: 1) Medium streaking: 3 (2*H*) Light arcing: 5 (2*H*: 1; 12*R*: 3; 12*H*: 1) Medium arcing: 2 (12*H*: 1; 16*H*: 1)

Storage (room temp.)

(i) All the heat-treated crystals that were originally 2*H* were restored to the same structure, *viz* 2*H*.

(ii) The higher polytypes (4*H*, 12*H*, 16*H*) and un types were not converted into 2*H*, whether present singly or in combination with 12*R*.

* un represents unidentified polytypes.

delayed. Thus they are most likely to form on the basal surfaces of the platelets of PbI_2-12*R* that would have formed in the initial stages of crystal growth. The crystal growth around such nuclei will end up in the formation of the polytype mixture PbI_2-(2*H* + 12*R*), with a relatively higher proportion of 2*H*, as actually observed.

However, even in the polytypes 12*R* and (4*H* + 12*R*), which together constitute 3/4 of the total number of cases, the existence of small amounts of the 2*H* nuclei cannot be ruled out, although they are not detected by X-ray diffraction. These nuclei will help to transform the crystal structure to 2*H* upon storage by rearrangement of the atomic layers, as explained earlier. The necessary layer displacement towards this end can occur by a deformation-fault mechanism (Pandey, 1988):

$$\begin{array}{ccccccc}
AB & CA & CA & BC & BC & AB & (12R) \\
 & \downarrow\downarrow & \downarrow\downarrow & \downarrow\downarrow & \downarrow\downarrow & \downarrow\downarrow & \\
 & AB & AB & CA & CA & BC & \\
 & & & \downarrow\downarrow & \downarrow\downarrow & \downarrow\downarrow & \\
 & & & AB & AB & CA & \\
 & & & & & \downarrow\downarrow & \\
 & & & & & AB & \\
AB & AB & AB & AB & AB & AB & (2H).
\end{array}$$

The arrows denote the layers where the faulting occurs. This transformation only involves displacements between I—I layers, which, owing to the sandwich structure of PbI_2, have bond strength ~100 times weaker than that for the I—Pb bond and hence they are far more prone to interlayer displacements.

One of the authors (AJ) is grateful to the University Grants Commission, India, for the award of a Senior Research Fellowship.

References

Choudhary, S. K. & Trigunayat, G. C. (1987). *J. Cryst. Growth*, **57**, 558-562.

Frey, F., Jagodzinski, H. & Steger, G. (1986). *Bull. Mineral.* **109**, 117.

Inomata, Y., Inoue, Z. & Kijima, K. (1969). *Yogyo Kyokai Shi*, **77**, 313.

Jain, A. & Trigunayat, G. C. (1995). *Z. Kristallogr.* **210**, 212-214.

Mehdi, S. & Trigunayat, G. C. (1989). *Phase Transit.* **16/17**, 417-424.

Minagawa, T. (1975). *Acta Cryst.* **A31**, 823-824.

Minagawa, T. (1981). *J. Phys. Soc. Jpn*, **50**, 902-906.

Palosz, B. (1983). *Phys. Status Solidi A*, **80**, 1-40.

Pandey, D. (1988). *Bull. Mater. Sci.* **10**, 125.

Prager, P. R. (1974). *Acta Cryst.* **A30**, 369-373.

Salje, E., Palosz, B. & Wruck, B. (1987). *J. Phys. C*, **20**, 4077-4096.

Vand, V. & Hanoka, J. I. (1967). *Mater. Res. Bull.* **2**, 241.