

features observed for the satellites may be related to a pseudoperiodic distribution of the different types of Mo₈ clusters along **b**. In spite of this deviation from an ideal modulated crystal, it seems reasonable to assume that the refinement results reported here give the main features of the structure without noticeable bias.

The authors are grateful to Mrs R. Aguiet and Mrs J. Chardon for their technical assistance.

References

B. A. FRENZ & ASSOCIATES, INC. (1982). *SDP Structure Determination Package*. College Station, Texas, USA.

- BROWN, I. D. & WU, K. K. (1976). *Acta Cryst.* **B32**, 1957–1959.
 CIANI, P., D'ALFONSO, G., FRENI, M., ROMITI, P. & SIRONI, A. (1982). *J. Chem. Soc. Chem. Commun.* p. 705.
 DOUDIN, B. (1985). Private communication.
 GOUGEON, P. & MCCARLEY, R. E. (1991). *Acta Cryst.* **C47**, 241–244.
 KILLEAN, R. C. G. & LAWRENCE, J. L. (1969). *Acta Cryst.* **B25**, 1750–1752.
 RELIGNY, H., LEDESERT, M., LABBE, P., RAVEAU, B. & MCCARROLL, W. H. (1990). *J. Solid State Chem.* **87**, 35–43.
 SMAALEN, S. VAN, (1987). *Acta Cryst.* **A43**, 202–207.
 WOLFF, P. M. DE (1977). *Acta Cryst.* **A33**, 493–497.
 WOLFF, P. M. DE, JANSEN, T. & JANNER, A. (1981). *Acta Cryst.* **A37**, 625–636.
 YAMAMOTO, A. (1982). *REMOS*. A computer program for the refinement of modulated structures. National Institute for Research in Inorganic Materials, Niihari-gun Ibaraki, Japan.

Acta Cryst. (1993). **B49**, 454–458

Impurity- and Temperature-Dependent Structural Transformations in Polytypic Crystals of CdI₂, PbI₂ and CdBr₂

BY S. K. CHAUDHARY

Department of Physics, University College, M. D. University, Rohtak 124001, India

(Received 6 May 1992; accepted 2 October 1992)

Abstract

Single crystals of polytypic materials CdI₂, PbI₂ and CdBr₂ were purified and grown at high temperatures by use of zone-refinement and Bridgman–Stockbarger techniques. The crystals were investigated by X-ray diffraction to ascertain how the purification of crystals influences the growth and polytypism of crystals. The results obtained were compared and correlated with various other studies made on crystals of these materials with special reference to the effect of purification, presence of impurities and the temperature.

Introduction

The phenomenon of polytypism has long engaged the attention of physicists and mineralogists and more recently it has attracted the attention of solid-state physicists because various polytypic modifications of the same substance have been found to possess different semiconducting, dielectric and photovoltaic properties (Tairov & Tsvetkov, 1983).

There are many physical factors associated with the growth of polytypes and a large number of explanations have been put forward to account for the phenomenon (Trigunayat & Verma, 1976). These have been based on such diverse considerations as

temperature, rate of crystallization, presence of impurities, thermodynamical factors, creation of dislocations during growth, internal rotations, electron energy *etc.* Of these, the presence of impurities is prominent and plays an important role in the growth and phase transformations of polytypes (Jepps & Page, 1984).

In the past three decades a considerable amount of work has been performed on the polytypism of CdI₂, PbI₂ and CdBr₂ crystals grown from solution, vapour or gel. Whereas this work has yielded significant results, not much attention has been paid thus far to the investigation of crystals grown from melt. The zone-refinement technique was employed here so that the degree of purification of the material could be controlled and single crystals of the material could be grown. X-ray diffraction (XRD) was used to study the nature of growth of the polytypes with special reference to the effects of purification, presence of impurities and temperature. The results are compared with others in the literature.

Experimental

The details of the zone-refinement system and growth processes of CdI₂ and PbI₂ crystals have been

described elsewhere (Chaudhary & Trigunayat, 1982, 1983). With increasing purification of the crystal ingot, its transparency gradually increased and its adhesion to the container walls decreased. Indeed, the extents of transparency and adhesion could be taken as reliable indices of the degrees of purification and single-crystal formation of the material. On account of the high vapour pressure of CdBr_2 at its melting point, which is about seven times the corresponding values for CdI_2 and PbI_2 , this material tended to evaporate. Therefore, to grow single crystals of this compound, the Bridgman–Stockbarger technique was employed. The purification of the material was achieved by repeated crystallizations. Details of the growth processes have been described by Chaudhary & Trigunayat (1986). The usual XRD oscillation method was employed for both polytype identification and detection of structural changes.

The crystals of CdI_2 , CdBr_2 and PbI_2 are known to exhibit syntactic coalescence of polytypes. Therefore, the two basal faces of each crystal were examined separately. Furthermore because of the large size of the crystal and the fact that those crystals sometimes also exhibit parallel growth of two or more polytypes on the same face, photographs were taken from at least four different parts of the same face in the region of back reflection.

Results and discussion

CdI_2 crystals

The formation of a single crystal requires eight zone passes. Six crystals, which involved more than 50 X-ray diffraction photographs, were investigated. All the crystals were found to be of the type $4H$. The crystals did not show any streaking or arcing on the X-ray photographs.

Marked structural changes in CdI_2 crystals due to length of storage were first observed by Trigunayat (1971), after storage at room temperature for 3 to 4 years. The observation stimulated a detailed investigation of the effect of heating on CdI_2 crystals.

The solid-state structural transformations of all CdI_2 polytypes into a common type $4H$ was reported for solution-grown crystals heated for just a few hours at about 530 K (Lal & Trigunayat, 1971, 1974). Thus, $4H$ may be regarded as a thermodynamically stable polytype of CdI_2 at high temperature, which agrees with the observation of only this polytype in melt-grown crystals. In melt growth, the temperature of the growing crystal is just below the melting point of the substance and any metastable structure formed will transform into a structure that has a minimum-energy configuration at that temperature. Sharma (1980) reported the vapour growth of CdI_2 crystals. All the crystals showed the spots of

$4H$ on the X-ray diffraction photographs, confirming the existence of only the most stable phase, $4H$, at high temperature.

In the above studies, the specific role played by the impurities remained unknown. Recently, specific studies on the effect of impurities on polytype growth were carried out by the incorporation of different impurities of known nature and of known small amounts into highly purified melt-grown CdI_2 crystals (Tyagi & Trigunayat, 1986, 1987, 1988). The dopants were chosen on the basis of their ionic radii, electronegativity/electropositivity and valency in relation to the structure of CdI_2 . Both cations (Pb, Sn, Ga, In) and anions (Br, Cl) were used. Each dopant formed a substitutional solid solution in cadmium iodide. The doping results in an increase in hardness and reduced cleavage of crystals. Differences in ionic sizes and crystal structures build up local internal stresses that are relieved by the production of dislocations and consequent stacking faults, which in turn affect polytype formation, and streaking and arcing on the X-ray photographs.

PbI_2 crystals

Lead iodide is of special interest because, although it is isostructural with CdI_2 , it displays polytypism on a much more restricted scale, and CdI_2 and PbI_2 when heated behave oppositely in respect of polytype transformations.

Crystals of three different degrees of purity were examined: (a) relatively less pure crystals (6–8 zone passes); (b) more pure crystals (12–14 zone passes); (c) very pure crystals (20 zone passes).

Nine crystals were examined from category (a), which involved 75 diffraction photographs. Of these, 51 (68%) showed the presence of $12R$. The same polytype appeared in the remaining cases but in coalescence with polytype $4H$.

Six crystals from category (b) were investigated, which involved 46 X-ray diffraction photographs. 36 (78%) showed the occurrence of $12R$ and 8 (18%) showed coalescence of this polytype with $4H$. Two (4%) showed coalescence of $12R$ and $2H$.

Similarly, five crystals were randomly chosen from category (c), which involved 39 photographs, all but one of which showed the polytype $12R$. One exceptional photograph showed coalescence with $4H$.

The frequencies of occurrence of various PbI_2 polytypes in crystals of different degrees of purity are given in Table 1.

After the crystals had been stored at room temperature for periods of 7 months or more, their structure was again examined by XRD. It was found that: (i) the structure of the crystals of category (a), stored for nearly 12 months, did not change; (ii) all but one of the crystals of category (b), stored for

Table 1. Frequencies of occurrence of various PbI_2 polytypes in crystals of different degrees of purity

Purity category	No. of zone passes	No. of crystals	Total No. of diffraction photographs	Structure		
				12R	12R+4H	12R+2H
(a)	6-8	9	75	51	24	0
(b)	12-14	6	46	36	8	2
(c)	20	5	39	38	1	0

nearly 9 months, transformed into 2H, the most common polytype of PbI_2 at room temperature; (iii) the structure of crystals of category (c), stored for nearly 7 months, did not change. The crystals were re-examined after a further storage of 5 years, when no further structural changes were observed in any of the three categories. Details of the observed structural changes are summarized in Table 2.

Like CdI_2 , the PbI_2 crystals did not show any streaking or arcing on X-ray photographs.

These observations clearly establish a link between the degree of purity of the material and phase transitions in polytypes. Empirically, the high-temperature common structure of PbI_2 is the polytype 12R (Minagawa, 1975). However, the observed admixture of polytype 4H in a substantial fraction of the crystals in categories (a) and (b) clearly proves that it represents a specially favourable metastable phase of lead iodide. This is not surprising since the crystal structure of 4H is nearest to the crystal structure of the stable high-temperature modification 12R, in the sense that the unit cell of 12R really consists of three unit cells of 4H rotated through 60° in succession. The decreasing content of 4H with purity can be accounted for as follows: Salje, Palosz & Wruck (1987), in an exhaustive study of $2H \rightleftharpoons 12R$ transition in PbI_2 through X-ray diffraction, differential scanning calorimetry and dielectric measurements, showed that nucleation centres for subsequent growth of 4H necessarily form around impurity particles. Since the crystals of category (a) consist of maximum impurities, they have the highest percentage of 4H in them; for extremely pure crystals of category (c), 4H vanishes.

The explanation for the different behaviours of the crystals of categories (a), (b) and (c) when stored at room temperature follows along similar lines. The presence of impurities plays a dual role in the polytypic crystals: (i) it produces local stresses in the crystal structure, giving rise to dislocations and stacking faults; (ii) it hinders the movement of dislocations and consequential retention of stacking faults (Singh & Trigunayat, 1989a). Crystals of category (c) are virtually free from impurities and therefore, during their prolonged storage at room temperature, they offer practically no scope for the creation of a nucleation centre of 2H. The transformation $12R \rightarrow 2H$ for crystals in category (a) is ruled out because 2H

Table 2. Structural changes in PbI_2 crystals after storage

Crystal No.	Initial structure	Final structure
(a) Relatively less pure crystals (6-8 zone passes); 12 month storage period		
(1A)	12R _r	12R _r
(1B)	12R _r	12R _r
(2A)	12R _r	12R _r
(2B)	12R _o	12R _o
(3A)	12R _r	12R _r
(4A)	12R _o	12R _o
(4B)	12R _o + 12R _r + 4H	12R _o + 12R _r + 4H
(5A)	12R _o + 4H	12R _o + 4H
(5B)	12R _o + 12R _r + 4H	12R _o + 12R _r + 4H
(6A)	12R _o + 12R _r + 4H	12R _o + 12R _r + 4H
(6B)	12R _r + 12R _o	12R _r + 12R _o
(7A)	12R _r + 12R _o	12R _r + 12R _o
(7B)	12R _r	12R _r
(8A)	12R _o	12R _o
(8B)	12R _o	12R _o
(9A)	12R _r + 12R _o + 4H	12R _r + 12R _o + 4H
(9B)	12R _r + 12R _o + 4H	12R _r + 12R _o + 4H
(b) More pure crystals (12-14 zone passes); 9 month storage period		
(1A)	12R _o	2H
(1B)	12R _o + 12R _r	2H
(2A)	12R _r + 12R _o	2H
(2B)	12R _r + 12R _o	2H
(3A)	2H + 12R _r	2H
(3B)	12R _o	2H
(4A)	12R _o	2H
(4B)	12R _r	2H
(5A)	12R _r	12R _r
(5B)	12R _o	12R _o
(6A)	12R _r + 4H	2H
(6B)	12R _r + 4H	2H
(c) Very pure crystals (20 zone passes); 7 month storage period		
(1A)	12R _o	12R _o
(1B)	12R _r	12R _r
(2A)	Face damaged	
(2B)	12R _r	12R _r
(3A)	12R _o	12R _o
(3B)	12R _o	12R _o
(4A)	12R _r	12R _r
(4B)	12R _r	12R _r
(5A)	12R _r	12R _r
(5B)	12R _r	12R _r

nuclei can form around impurity particles but their growth is seriously hindered by the presence of large amounts of impurities. The situation is only favourable for crystals in category (b), which contain intermediate amounts of impurities. Here, scope exists for both the formation and the growth of nuclei. Consequently, they can transform back into the stable room-temperature modification 2H, as actually observed.

Some results have been reported on the effect of impurities on polytypism of SiC and ZnS. Lundqvist (1948), employing spectrochemical and X-ray powder analysis, and Hayashi (1960), employing chemical and X-ray powder analysis, concluded that the formation of small-period polytypes 6H, 15R and 4H was related to their aluminium content. However, in a subsequent extensive study, Knippenberg (1963) failed to observe such a correlation for SiC

crystals grown with different proportions of aluminium at constant temperature, which led him to conclude that the suspected impurity–structure correlation might really be a temperature–structure relationship. Later, Bootsma, Knippenberg & Verspui (1971) inferred that the nature and amount of impurity content, temperature and pressure had a combined influence on the formation of common SiC types $6H$, $15R$ and $4H$; for higher polytypes, defects in the initial nuclei were also held responsible. Kozielski (1976) stated that, under doping with Al at 0.01% concentration the structure of ZnS crystals is transformed from $3C$ through intermediate polytype structures to $2H$. The transformation broadly follows the scheme $3C \rightarrow 10H \rightarrow 6H \rightarrow$ disordered structure $\rightarrow 2H$.

Recently, a systematic study of phase transformation with temperature was undertaken in single crystals of lead iodide grown in gel (Soudmand & Trigunayat, 1989). The crystals of polytype $2H$ were found to transform ultimately into $12R$ after being heated at 423 K. It was further reported that addition of a small amount of AgI as impurity promotes the incidence of polytypism and the process of phase transformation is appreciably altered; this is well explained by the difference in ionic radii of lead and silver.*

CdBr₂ crystals

Eight crystals, involving 58 X-ray photographs, exclusively showed the diffraction spots of $6R$, which is a common polytype of CdBr₂ at room temperature. Streaking and arcing was observed in these crystals, although only in a few cases.

In melt growth, a steady supply of energy is available and it is expected that most dislocations and random stacking faults will normally be eliminated from the crystals. Thus, the CdI₂ and PbI₂ crystals grown from well purified zone-refined material are likely to have no streaking or arcing on their X-ray photographs, as actually observed. However, this is not the case for CdBr₂, since these crystals were grown by Bridgman–Stockbarger technique and hence are not as pure. The impurities they contain act as obstacles to the movement of dislocations and thus hinder the elimination of dislocations and stacking faults, giving rise to streaking and arcing on the X-ray diffraction photographs.

* In the present work, the manufacturers (E. Merck, Germany) of the CdI₂ had indicated the presence of Fe, Ag, Na and K in the raw material. An atomic absorption spectroscopy test revealed the total absence of Fe and Ag and only nominal presence ($\ll 1$ in 10^6) of Na and K in the well purified CdI₂ crystals. Unfortunately, on account of insurmountable experimental difficulties, no similar detection of impurities could be carried out for the PbI₂ and CdBr₂ crystals.

These features are also partly attributable to the structural characteristic of CdBr₂ crystals: in addition to close-packed basal planes (0001), there exist equivalent nonbasal close-packed planes (10 $\bar{1}$ 2) in the structure along which slip can occur with equal ease and thus the chance of creation of edge dislocations and stacking faults is increased (Agrawal & Trigunayat, 1970).

Recently, Singh & Trigunayat (1989b), in their study of highly pure CdBr₂ crystals grown by vertical zone refinement, reported the total absence of streaking and arcing on the X-ray photographs.

Experiments on heating solution-grown CdBr₂ crystals were conducted by Sharma (1980). When higher unidentified polytypes of crystals were heated at about 473 K for 1 h, they changed to $6R$ without any disorder on their X-ray photographs.

Evidence of the formation of polytypes due to impurities also exists in the literature on other materials (Jepps & Page, 1984).

Through a careful study of kinetics and thermodynamics of processes of polytype growth and of various growth parameters (temperature, nonstoichiometry, impurities, substrate surface *etc.*), limited but remarkable success has been achieved in the controlled growth of the small-period structures $3C$, $4H$ and $6H$ of silicon carbide (Tairov & Tsvetkov, 1983). As the concepts of polytype formation become clearer, the scope for such controlled growth of polytypes will widen.

Thanks are due to Dr Harjeet Kaur for her kind cooperation during this work.

References

- AGRAWAL, V. K. & TRIGUNAYAT, G. C. (1970). *Acta Cryst.* **A26**, 426–429.
- BOOTSMA, G. A., KNIPPENBERG, W. F. & VERSPUI, G. (1971). *J. Cryst. Growth*, **8**, 341–353.
- CHAUDHARY, S. K. & TRIGUNAYAT, G. C. (1982). *J. Cryst. Growth*, **57**, 558–562.
- CHAUDHARY, S. K. & TRIGUNAYAT, G. C. (1983). *J. Cryst. Growth*, **62**, 398–400.
- CHAUDHARY, S. K. & TRIGUNAYAT, G. C. (1986). *J. Cryst. Growth*, **73**, 543–545.
- HAYASHI, A. (1960). *J. Mineral. Soc. Jpn*, **4**, 363–371.
- JEPPE, N. W. & PAGE, T. F. (1984). *J. Prog. Cryst. Growth Charact.* **7**, 259–306.
- KNIPPENBERG, W. F. (1963). *Philips Res. Rep.* **18**, 161–274.
- KOZIELSKI, M. J. (1976). *Bull. Acad. Pol. Sci. Ser. Sci. Chim.* **24**(5), 367–375.
- LAL, G. & TRIGUNAYAT, G. C. (1971). *J. Cryst. Growth*, **11**, 177–181.
- LAL, G. & TRIGUNAYAT, G. C. (1974). *J. Solid State Chem.* **9**, 132–138.
- LUNDQVIST, D. (1948). *Acta Chem. Scand.* **2**, 177–191.
- MINAGAWA, T. (1975). *Acta Cryst.* **A31**, 823–824.
- SALJE, E., PALOSZ, B. & WRUCK, B. (1987). *J. Phys. C*, **20**, 4077–4096.

- SHARMA, G. L. (1980). PhD thesis, IIT Delhi, India.
- SINGH, K. & TRIGUNAYAT, G. C. (1989a). *Phase Transit.* **16/17**, 529–535.
- SINGH, K. & TRIGUNAYAT, G. C. (1989b). *J. Cryst. Growth*, **97**, 863–865.
- SOUDMAND, M. & TRIGUNAYAT, G. C. (1989). *Phase Transit.* **16/17**, 417–424.
- TAIROV, Y. M. & TSVETKOV, V. F. (1983). *Crystal Growth and Characterization of Polytype Structures*, edited by P. KRISHNA, pp. 111–161. Oxford: Pergamon Press.
- TRIGUNAYAT, G. C. (1971). *Phys. Status Solidi A*, **4**, 281–303.
- TRIGUNAYAT, G. C. & VERMA, A. R. (1976). In *Physics and Chemistry of Materials with Layered Structures*, Vol. 2, edited by F. LEVY. Dordrecht: Reidel.
- TYAGI, U. P. & TRIGUNAYAT, G. C. (1986). *Cryst. Res. Tech.* **21**, 891–895.
- TYAGI, U. P. & TRIGUNAYAT, G. C. (1987). *Acta Cryst.* **A43**, C-309.
- TYAGI, U. P. & TRIGUNAYAT, G. C. (1988). *Acta Cryst.* **C44**, 1157–1162.

Acta Cryst. (1993). **B49**, 458–463

Small-Angle X-ray Scattering Study of Precipitation in a Cu–2 at.% Co Alloy

BY P. ANCRENAZ

Centre de Recherches et Etudes d'Arcueil, 16 bis Avenue Prieur de la Côte d'Or, 94114 Arcueil CEDEX, France

C. SERVANT

Laboratoire de Métallurgie Structurale, UA CNRS 1107, Université de Paris-Sud, Bâtiment 413, 91405 Orsay CEDEX, France

AND O. LYON

Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Université de Paris-Sud, Bâtiment 209, 91405 Orsay CEDEX, France

(Received 30 December 1991; accepted 29 October 1992)

Abstract

The unmixing at 923 K of a binary alloy Cu–2 at.% Co was studied by anomalous small-angle X-ray scattering performed at the Co *K*-absorption edge and transmission electron microscopy. For ageings of 3 and 120 h a marked anomalous effect was observed. Experimental curves were fitted with the help of a model that took into account the radius of precipitates, their volume fraction and the radius of excluded spheres. X-ray absolute scattered-intensity measurements allowed us to determine the cobalt concentration in precipitates.

1. Introduction

The Cu–Co binary system is difficult to investigate by the classical small-angle X-ray scattering technique due to the very small difference in atomic number between Cu and Co. To increase the contrast, use can be made of the anomalous effect.

The present study aims at determining the different stages of the unmixing of a Cu–2 at.% Co alloy aged at 923 K for different ageing times by the anomalous small-angle X-ray scattering technique

(ASAXS) performed at the Co *K* edge and transmission electron microscopy (TEM).

2. Experimental procedure

2.1. Sample preparation and heat treatment

The Cu–2 at.% Co alloy becomes single phased by homogenization treatment at 1238 K for 2 h under an argon atmosphere, followed by water quenching. Precipitation was performed at 923 K, under an argon atmosphere, for an ageing time varying between $\frac{1}{2}$ and 120 h.

The thin foils used both for ASAXS experiments and for TEM observations were obtained from samples by electrothinning. Final thickness was about 15 to 25 μm . Polishing was carried out at 293 K in a solution containing 30 cm^3 pure water and 70 cm^3 orthophosphoric acid, with a potential difference of 1 V.

2.2. TEM

The TEM and microdiffraction experiments were carried out with a JEOL 120C microscope operating at 120 kV.