pared with the smaller, heavier rare-earth elements. In general the difference in coordination between the light and the heavy rare-earth elements can be observed only in compounds where the rare-earth element is a minority component such that every rare-earth element is completely surrounded by atoms of another kind.

In Fig. 5, an extension of a diagram given by McMasters, Gschneidner, Bruzzone & Palenzona (1971), the coordination numbers of the rare-earth element for all the different RAu structure types are plotted as a function of the R/Au ratio on a logarithmic scale. Large and small rare-earth compounds of composition R_2Au have the same structure types and the same coordination.

Only with smaller R/Au ratios does one find different structure types and coordinations for the rare-earth components. The rare-earth coordinations in the two RAu_6 structure types follow the expected trend.

Replacing Au with another element of the same group of the periodic system one finds that RAg_6 compounds do not exist, but $CeCu_6$ is known (Cromer, Larson & Roof, 1960). Copper is smaller than gold and consequently the coordination polyhedron around Ce has 19 Cu atoms.

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References

BUSING, W. R., MARTIN, K. O., LEVY, H. A., BROWN, G. M., JOHNSON, C. K. & THIESSEN, W. E. (1971*a*). *ORFFE*3. Oak Ridge National Laboratory, Oak Ridge, Tennessee.

BUSING, W. R., MARTIN, K. O., LEVY, H. A., ELLISON, R. D., HAMILTON, W. C., IBERS, J. A., JOHNSON, C. J. & THIESSEN, W. E. (1971*b*). *ORXFLS*3. Oak Ridge National Laboratory, Oak Ridge, Tennessee.

CROMER, D. T., LARSON, A. C. & ROOF, R. B. (1960). *Acta Cryst.* **13**, 913–918.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

FLACK, H. D., MOREAU, J. M. & PARTHÉ, E. (1974). *Acta Cryst.* B**30**, 820–821.

FRANK, F. C. & KASPER, J. S. (1958). *Acta Cryst.* **11**, 184–190.

International Tables for X-ray Crystallography (1967). Vol. II. Birmingham: Kynoch Press.

International Tables for X-ray Crystallography (1968) Vol. III. Birmingham: Kynoch Press.

KASPER, J. S. (1956). *Theory of Alloy Phases*, pp. 264-276. Cleveland: ASM.

LEVY, H. A. & ELLISON, R. D. (1960). *Acta Cryst.* **13**, 270–271.

MCMASTERS, O. D. & GSCHNEIDNER, K. A. JR (1973). *J. Less-Common Metals*, **30**, 325–342.

MCMASTERS, O. D., GSCHNEIDNER, K. A. JR, BRUZZONE, G. & PALENZONA, A. (1971). *J. Less-Common Metals*, **25**, 135–160.

MAIN, P., WOOLFSON, M. M. & GERMAIN, G. (1972). *LSAM, a System of Computer Programs for the Automatic Solution of Centrosymmetric Crystal Structures*. Department of Physics, Univ. of York, York, England.

MOREAU, J. M. & PARTHÉ, E. (1972). *C. R. Acad. Sci. Paris*, **274**, 823–826.

PEARSON, W. B. (1972). *The Crystal Chemistry and Physics of Metals and Alloys*. Vol. 3. London: John Wiley.

STEEB, S., GEBHARDT, E. & REULE, H. (1972). *Mh. Chem.* **103**, 716–735.

YVON, K., JEITSCHKO, W. & PARTHÉ, E. (1969). *A Fortran* IV *Program for the Intensity Calculation of Powder Patterns* (1969 version). Univ. de Genève, Laboratoire de Cristallographie aux Rayons X.

Acta Cryst. (1974). B**30**, 1748

Structural Transformations in Lead Iodide Crystals

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Solid-state phase transformations involving basic and long-period lead iodide polytypes have been investigated. The phase transformations have been initiated by annealing the crystals under a vacuum of 10^{-3} to 10^{-4} torr at a temperature of 260 ± 20 °C for a period of 6 h. While the basic $2H$ structure undergoes transformations on each annealing run leading to the creation of new polytypes of higher periodicities, the same is not true for the high-period polytype $12H$. The polytype $12H$ does not show any clear-cut change under repeated annealing.

Introduction

In the past 20 years, much attention has been paid to the phenomenon of polytypism. From an applied point of view, the importance of these studies lies in the preparation of polytypes of known periodicities which can be used as substitutes for various materials with specific properties (dielectric constant in the case of lead iodide) differing on a known scale. One of the easiest ways to achieve this is through phase transformations where, starting from one polytype, one can develop other polytypes after inducing phase transformations. In spite of its obvious importance very little such work has been done although some has appeared recently. In the case of lead iodide crystals, the first studies regarding phase transformations were reported by Prasad & Srivastava (1973). Structural transformations involving several low-identity-period polytypes such as $2H$ and $4H$ were reported. However, studies of transformation involving high-period polytypes were not included in this initial investigation. The aim of the present communication is to report the phase-transformation studies in lead iodide polytypic crystals involving high-period polytypes. Order–disorder changes have also been encountered. It has been shown that as far as the transformation of long-period lead iodide polytypes is concerned, the results obtained in the present study are remarkably different from the results of similar previous investigations carried out for other polytypic materials.

Experimental results

The method of growth of the crystals and the details of the annealing treatment (which induces phase transformations) have already been described (Prasad & Srivastava, 1973). While the annealing mode was exactly the same as that described previously (working temperature $= 260 \pm 20$°C, duration of anneal $= 6$ h, vacuum $= 10^{-3} - 10^{-4}$ torr), the method of growth differed slightly in the sense that Ag impurities were added to the mother liquor, in order to initiate the formation of long-period polytypes (Hanoka & Vand, 1968).

Figs. 1–8 are 15° a-axis oscillation photographs taken with Cu $K\alpha$ radiation with a camera of 3 cm radius.

Fig. 1 represents the long-period polytype isolated from a batch of 30 crystals. The polytype was identified as $12H$. Besides the discrete sharp spots, a feeble streak running along the c^* axis in a $10.l$ row is also visible in Fig. 1. This implies that besides the $12H$ polytype a superimposed disordered structure is also present. Fig. 2 is an oscillation photograph of the same crystal as that represented by Fig. 1 but corresponding to the opposite face of the crystal. The polytype on this face was identified as the basic $2H$ structure. Other crystals of the batch from which the above crystal was extracted were found to have either basic $2H$ structure or else $12H$ similar to that shown in Fig. 1. There were as many as six $12H$ polytypes in the batch of crystals under study. This result is in marked contrast to the observations for other polytypic substances such as cadmium iodide, zinc sulphide and silicon carbide, where in a batch of crystals a wide variety of polytypes is found to exist. In lead iodide the crystals grown from a pure phase are all found to be basic $2H$ structures and the long-period polytypic structures appear only when impurities are added to the solution from which the crystals are grown. The present observation seems to suggest that the $12H$ polytype is a particular impurity-induced phase of the basic structure $2H$.

The crystal representing the $12H$ polytypic structure was annealed in the previously described way for inducing phase transformations. Fig. 3 shows the oscillation photograph of the crystal face corresponding to Fig. 1. A comparison of Figs. 1 and 3 makes it evident that no structural change has taken place as a result of annealing. Fig. 4 represents the oscillation photograph of the crystal face corresponding to Fig. 2 after annealing. A comparison of Figs. 2 and 4 reveals that a phase transformation has taken place. Identification of the transformed structure shows that it corresponds to a $4H$ structure; there is some superimposed disorder represented by the appearance of a faint streak. We thus have a transformation $2H \rightarrow (4H + \text{disorder})$ for the crystal face corresponding to the basic structure $2H$. A second anneal was undertaken in the hope of getting a possible transformation for the polytype $12H$, which did not transform during the first anneal. Figs. 5 and 6 represent the oscillation photographs of the two crystal faces corresponding to the $12H$ and $(4H + \text{disorder})$ structures after the second anneal. These figures show that the $12H$ polytypic structure has again not changed but the $(4H + \text{disorder})$ structure has transformed to a $12R$ structure. Since no streak accompanies this change, we have a transformation represented by $4H$ (disordered) $\rightarrow 12R$ (ordered). The results of another anneal (the third) are shown in Figs. 7 and 8. Fig. 7 corresponds to Figs. 1, 3 and 5 and it is clear that the polytype $12H$ remains unchanged even after the third anneal. It should be mentioned that the arcing and smearing of spots appearing in Fig. 7 do not represent any lattice disorders similar to those described by Tiwari, Prasad & Srivastava (1973). Fig. 8, which corresponds to Figs. 2, 4 and 6, reveals that we have a transformation where the $12R$ structure changes to the $18R$ structure, which is again ordered.

In the present investigation the above transformation characteristic, *i.e.* the unchangeability of the high period polytype, was confirmed for other $12H$ crystals extracted from the same batch in which the reported $12H$ was found. The repeated occurrence of the same polytype in a batch of lead iodide crystals was verified for other batches also. The polytypes did not show any change in shape after the annealing treatments. This suggests that the transformations observed in the present study were not martensitic in character.

Discussion

Although the polytypic transformations in various materials differ in detail, one common feature is the role of stacking faults in inducing transformations (Tiwari & Srivastava, 1972; Krishna, Marshall & Ryan, 1971). In the case of lead iodide, the present authors have shown previously that in the crystals representing the pure phase which correspond to the basic polytype the transformations take place by

Fig. 1. The first layer line of lead iodide $12H$ polytype (before annealing).

Fig. 2. The first layer line of the $2H$ polytype found on the opposite face to the $12H$ polytype (Fig. 1) (before annealing).

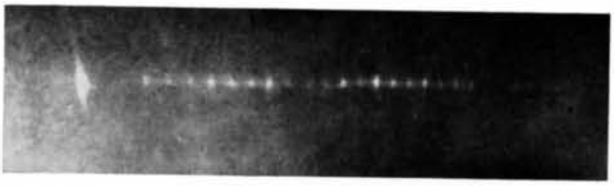

Fig. 3. The same crystal as in Fig. 1 after annealing for 6 h. A comparison of Figs. 1 and 3 shows that transformation of the $12H$ polytype has not taken place.

Fig. 4. The crystal face corresponding to Fig. 2 after annealing for 6 h. A comparison of Figs. 2 and 4 shows that a transformation from $2H$ to $4H$ plus some disorder has taken place.

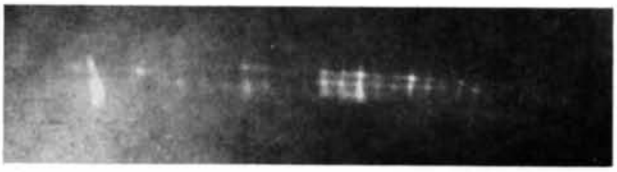

Fig. 5. The crystal face corresponding to Figs. 1 and 3 after annealing for 6 h for the second time. A comparison of this photograph with Figs. 1 and 3 shows that there is no clear-cut change in the $12H$ structure.

Fig. 6. The face opposite to that in Fig. 5. A comparison with Fig. 4 shows that a further transformation, *i.e.* ($4H$ + disorder) → $12R$ (ordered) has taken place.

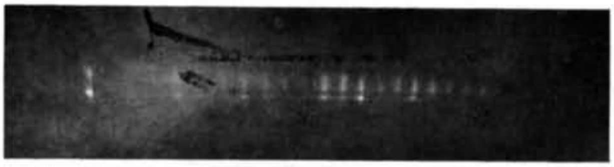

Fig. 7. The crystal face corresponding to Figs. 1, 3 and 5 ($12H$ polytype) after annealing for 6 h for the third time. No noticeable change in the structure is observed.

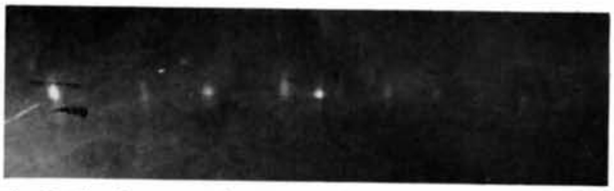

Fig. 8. The face opposite to that of Fig. 7. A comparison with Fig. 6 shows that a further transformation, $12R \rightarrow 18R$ has taken place.

[*To face p.* 1749

nucleation, propagation and redistribution of stacking faults in the basic structure. The present transformation sequences involving the basic $2H$ pure phase, *i.e.* the sequences (i) $2H \rightarrow (4H+\text{disorder})$ (Figs. 2 and 4), (ii) $(4H+\text{disorder}) \rightarrow 12R$ (Figs. 4 and 6) and (iii) $12R \rightarrow 18R$ (Figs. 6 and 8), can easily be understood on the basis of the previously described mode of changes in the existing stacking fault sequences. The impurity phase $12H$ polytype does not show any change in its periodicity even on repeated annealings. However, there seems to be some change in the intensity sequence of the $12H$ polytype on annealing (Figs. 1, 5 and 7). Since the change in the intensity sequence of Figs. 1, 5 and 7 is not significant, it is difficult to say with certainty that they represent different $12H$ polytypes, *i.e.* the polytypes having 12 layers each but with different arrangement of layer sequences. Calculation of structure factors in cadmium iodide and lead iodide shows that the intensity sequences are rather drastically affected even for the change of one iodine and the corresponding metal layer (Prasad, 1971). It thus appears that all the present $12H$ polytypes have the same layer sequence.

The unchangeability of the long-period $12H$ polytype when annealed, as observed in the present investigation, represents an interesting result since it suggests that the long-period lead iodide polytypes, in marked contrast to the basic $2H$ polytype, do not undergo any transformation on annealing. The present result, the unchangeability of the long-period polytype, is also at variance with the results on transformation of long-period polytypes in other polytypic materials (Daniels, 1966; Mardix, Kalman & Steinberger, 1968; Lal & Trigunayat, 1970; Tiwari & Srivastava, 1972). As described previously, in keeping with the results of Hanoka & Vand (1968), a long-period polytype of lead iodide represents an impurity-induced phase. This is one of the reasons why lead iodide was considered to be non-polytypic for a long time.

Long-period polytypes are formed only when small quantities of impurities, usually silver or silver iodide, are added to the mother liquor from which the crystals form. The occurrence of the same polytypic crystal $12H$ in a batch of crystals grown under the same experimental conditions suggests that the impurities were not only responsible for the nucleation of this phase but that the identity period and the structure of the polytype were also crucially dependent on these impurities. It appears that the impurity content for the particular growth was such that it nucleated the same ordered sequence in the basic $2H$ structure whenever it influenced the stacking sequence of the basic $2H$ polytype. It may be emphasized that the occurrence of the same polytypic structure in a whole batch of crystals, is peculiar to lead iodide crystals. For other polytypic materials where impurities do not have any known influence on the nucleation of a polytype, a batch of crystals exhibits a variety of polytypes and not the repeated occurrence of the same polytype. Taking the observed $12H$ polytype to be an impurity-induced phase, the unchangeability of the polytype on annealing indicates that the existing stacking faults which are responsible for the formation of the polytype do not undergo any change on annealing. Also, additional stacking faults are not created on annealing. Both these facts suggest that the stacking-fault energy at the transformation temperature for the impurity-induced phases is different from the pure basic phases. The fact that the existing faults do not change suggests that the activation energy for partial movement is comparatively high and the fact that additional faults are not created indicates that the stacking-fault energy for impurity-induced phases is also high. Taking the above facts into account the unchangeability of the $12H$ polytypic structure can be reasonably well understood. The polytype $12H$ does not undergo any transformation because on annealing neither do the existing faults undergo any rearrangement nor are additional faults created.

References

Daniels, B. K. (1966). *Phil. Mag.* **14**, 487–500.

Hanoka, J. I. & Vand, V. (1968). *J. Appl. Phys.* **39**, 5288–5297.

Krishna, P., Marshall, R. C. & Ryan, C. E. (1971). *J. Cryst. Growth*, **8**, 129–131.

Lal, G. & Trigunayat, G. C. (1970). *Acta Cryst.* A**26**, 430–431.

Mardix, S., Kalman, Z. H. & Steinberger, I. T. (1968). *Acta Cryst.* A**24**, 464–469.

Prasad, R. (1971). Ph. D. thesis, Banaras Hindu Univ.

Prasad, R. & Srivastava, O. N. (1973). *J. Cryst. Growth.* **19**, 11–17.

Tiwari, R. S., Prasad, R. & Srivastava, O. N. (1973). *Acta Cryst.* **29**, 154–156.

Tiwari, R. S. & Srivastava, O. N. (1972). *J. Appl. Cryst.* **5**, 347–352.