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Dendritic Growth of PbI_2 Single Crystals and Study of their Polytypism and Growth Features

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Abstract

Dendritic single crystals of highly purified lead iodide were grown from the vapour phase in vacuum. XRD was employed to characterize them and to study their polytypism and related behaviour. Most crystals were found to consist of the common polytype $12R_O$ and $12R_R$. Streaking of the reflections was not seen in the X-ray photographs, but nearly 12% of the photographs showed arcing of the reflections. The surface microtopographic study of the basal (0001) faces of the crystals revealed typical dendritic growth features. Layer-by-layer growth by two-dimensional nucleation was frequently observed, while spiral growth was not observed at all.

Introduction

The polytypism and related phenomena of lead iodide crystals have been extensively investigated in the last few decades. The crystals studied so far have mostly been grown from the gel and the vapour as hexagonal platelets. Recently, a detailed study of polytypism and phase transformation of lead iodide crystals with this platelet-forming habit has been carried out by Mehdi (1990) and Mehdi & Trigunayat (1989) by heating the crystals during growth from the gel. It is now well established that the formation of polytypes is related to crystal habit (Terhell, 1983; Prager, 1983; Cochrane, 1967).

We have successfully grown dendritic crystals of lead iodide to study their polytypism and related phenomena. A survey of the past literature has revealed that this is possibly the first time that dendritic crystals of lead iodide have been grown. The aim of the present work has been twofold: (i) to investigate the crystals from the point of view of their polytypism and (ii) to unravel the nature of dendritic growth itself in a layered MX_2-type material such as PbI_2. The X-ray diffraction oscillation method has been employed for characterizing the crystals and for studying the polytypism and related phenomena of the crystals. The results have been discussed in the light of current advances in the knowledge of polytypism of crystals. Some of the important aspects of dendritic growth are the formation of branches, their spacing and orientation with respect to the stem (Gonda, Nakahara & Sei, 1990) and growth rate (Banbieri & Langer, 1989; Amar, 1990), which have been investigated over the last few decades. For the present work we have carried out optical and scanning-electron-microscope studies on the basal (0001) faces of the dendritic crystals to throw more light on such growth features.

Experimental

Reagent-grade lead iodide (purity 99%, supplied by Aldrich, England) was highly purified by the zone-refining technique. The experimental set-up and process were similar to that used by earlier workers (Nigli, Chadha, Trigunayat & Bagai, 1987). However, modifications have been made to the experimental set-up that have considerably helped in minimizing the melt-zone width and in rendering flatter the solid-melt interface, which in turn have led to an improved purification of the material (Kumar & Trigunayat, 1991*a*). The zone speed was maintained at 1.2 cm h^{-1}. 15 zone passes were made. Subsequently, the highly pure initial and middle portions of the ingot were employed for crystal growth. The dendritic crystals of lead iodide were grown from vapour in a quartz tube (labelled 2 in Fig. 1) of diameter 40 mm, which was placed symmetrically in a cylindrical furnace (1). The charge was taken in a small quartz cup (3) and placed inside the tube at the middle of the furnace as shown in Fig. 1. The tube was then evacuated to a pressure of the order of 1 to 0.1 Pa. The temperature at the charge was raised to 823 K. The variation of temperature along the axis of the furnace is shown in Fig. 2. Within 6-7 h dendritic crystals were seen

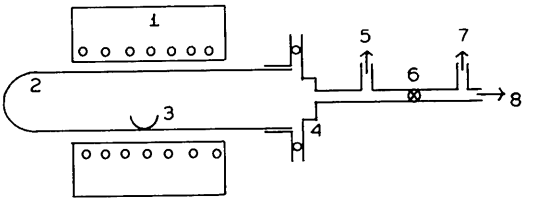

Fig. 1. Schematic diagram of experimental set-up used for dendritic crystal growth. (1) Furnace, (2) quartz tube, (3) quartz cup, (4) airtight metallic flange, (5) Pirani gauge, (6) stop cock, (7) air admittance, (8) rotary pump.

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to have grown about 10 cm from the charge, on both sides, in the temperature range 703–623 K. The tips of the dendrites were found to be sticking to the walls of the tube. They were collected on soft tissue paper.

These crystals were then investigated for their polytypism and related phenomena. For this purpose, X-ray oscillation photographs were taken about the *a* axis of a crystal. The range of oscillation was so chosen that the angle made by the *c* axis of the crystal with the incident X-ray beam varied between 25 and 40°. This range provides a long succession of 10.*l* reflections along a layer line, which is very useful for rapid identification of the polytype contained in the crystal. Since the PbI_2 crystals are known to contain different polytypes on the two basal faces of the crystal, as in other parts of the crystal, both faces of each dendrite were exposed to the X-rays and for each face oscillation photographs were taken from four or five different portions of the dendrite. All the photographs were recorded on a cylindrical camera of radius 3 cm, employing Ni-filtered Cu $K\alpha$ radiation.

For the study of surface growth features, the basal (0001) faces of the crystals were initially observed through an optical microscope. Subsequently, to obtain higher resolution and magnification, they were studied through a scanning electron microscope (model SEM JEOL HSM 840). For this the crystals were stuck on brass blocks by adhesive and then were sputtered with gold. This sputtering was needed due to the low electrical conductivity of lead iodide.

Results and discussion

The crystals were leaf-shaped, soft and yellow. They measured nearly 8 × 4 mm laterally (in the *c* plane) and were nearly 100 μm thick. A complete PbI_2 dendrite is shown in Fig. 3.

All the X-ray photographs showed a total absence of streaking, in which the neighbouring reflections are interconnected through streaks of varying intensity (Trigunayat, 1971). A small number of oscillation photographs exhibited arcing, in which each reflection appears as a small arc that consists of two or more diffraction spots (Trigunayat, 1971). Nearly all the photographs showed reflections of the twelve-layered rhombohedral polytype 12*R*. The polytypes $12R_O$ and $12R_R$ (the subscripts '*O*' and '*R*' refer to the 'obverse' and 'reverse' settings, respectively, of the rhombohedral unit cell) are structurally equivalent and one can be converted into the other merely by a rotation of ±60° about the *c* axis. In most cases the intensities of $12R_O$ and $12R_R$ spots were not found to be equal, thus implying that one of them had grown in a larger proportion in the crystal. The results of the X-ray diffraction study are summarized below:

number of dendritic crystals studied: 16
number of oscillation photographs taken: 92
break down of the X-ray photographs of various polytypes:

$$12R_O + 12R_R : 91\ (99\%)$$
$$4H + 12R_O + 12R_R : 1\ (1\%)$$

photographs showing streaking: nil
photographs showing arcing: 11 (12%).

It should be noted that the occurrence of the 12-layered rhombohedral structure (12*R*), which is known to be a common polytype of lead iodide at high temperatures (Salje, Palosz & Wruck, 1987) was 99%. Fig. 4 depicts an oscillation photograph showing the reflections of $12R_O$ and $12R_R$ (marked by arrows). The four-layered hexagonal polytype 4*H* occurred in just one case (Fig. 5).

It is generally believed that higher (or lower) polytypes of a material usually result from the creation and subsequent ordering of stacking faults in the structure of the basic polytype. The stacking faults, in turn, are believed to result from the movement of

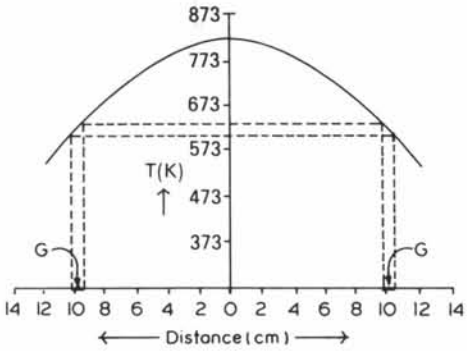

Fig. 2. Variation of temperature along the tube axis in the furnace employed for crystal growth. Crystals grow nearly 10 cm (*G*) from the charge (0) on both sides, in the temperature range 603–623 K.

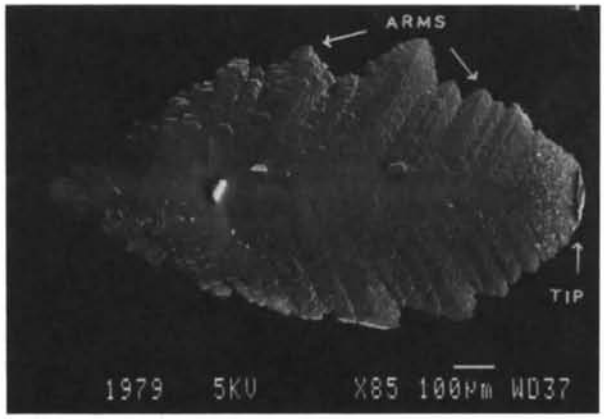

Fig. 3. Scanning electron micrograph of a PbI_2 dendrite.

dislocations that usually arise from the existence of internal stresses in the crystal. A major source of the internal stresses is known to be the randomly distributed impurities in the body of the crystal (Chaudhary & Trigunayat, 1987; Tairov & Tsvetkov, 1984). The observed absence of polytypes other than the basic $12R$ (except in one case, in which $4H$ reflections have been observed; see Fig. 5) suggests that, despite the rapid dendritic growth, the local internal stresses in the basic structure were not widely spread. This was expected for the extremely pure material employed for crystal growth in the present work. The observed absence of streaking on X-ray photographs implies a near total absence of random stacking faults in the crystals, which further confirms the very low density of impurities in the crystals. Arcing has been observed on some X-ray photographs, but the percentage occurrence of arcing was low, *viz* 12%, and the observed arcs had very small lengths. An example is shown in Fig. 6. Since arc formation results from the movement of edge dislocations into small-angle-tilt boundaries, the small arc length indicates a small angle of tilt and therefore a low density of dislocations in the structure. It is noteworthy that, despite the apparent roughness seen on their surfaces and the departure in shape from that of the conventional hexagonal platelets, the PbI_2 dendrites have been found to be good single crystals from a structural point of view.

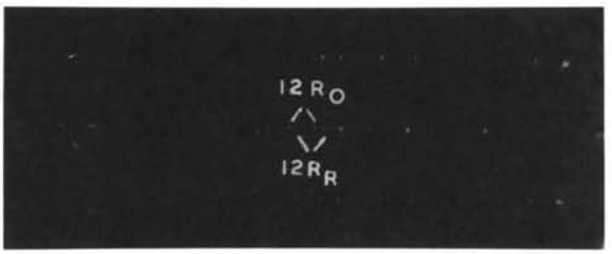

Fig. 4. *a*-axis 15° oscillation photograph of a dendritic single crystal, showing reflections of $12R_R$ and $12R_O$ (one reflection for each polytype is marked by an arrow), camera radius 3 cm; Cu $K\alpha$ radiation.

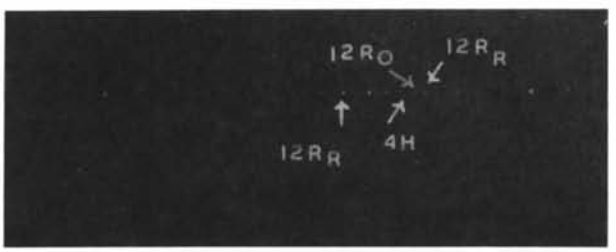

Fig. 5. *a*-axis 15° oscillation photograph of a dendrite, showing reflections of $4H$, $12R_R$, $12R_O$. Other conditions: same as in Fig. 4.

Fig. 6. *a*-axis 15° oscillation photograph of a dendrite showing arcing. Other conditions: same as in Fig. 4.

A striking feature of the optical study of the crystals has been that a well defined stem was not seen in most of the PbI_2 dendrites, in contrast to CdI_2 dendrites previously grown by us (Kumar & Trigunayat, 1991*b*). However, stems were seen in the primary arms situated relatively close to the tip of a dendrite. Also, in contrast to the CdI_2 dendrites, the spaces between the dendritic arms (both primary and secondary) were filled. The arms situated farther from the tip were slightly separated from one another. The primary arms made an angle of 60° with the main stem (not actually seen but thought of as joining the tip and the farthest opposite point).

The most commonly observed features on the surface of a dendrite have been a large number of zigzag growth steps. An example is shown in Fig. 7. The steps are inclined to each other at an angle of 120°. The most favourable directions for the steps are expected to be in the directions of close packing. The PbI_2 crystals have three equivalent close-packed directions, *viz* $[11\bar{2}0]$, $[1\bar{2}10]$ and $[\bar{2}110]$ or $[\bar{1}\bar{1}20]$, $[\bar{1}2\bar{1}0]$ and $[2\bar{1}\bar{1}0]$, which are inclined at 120° to one another. 'Bunching' of growth steps, *i.e.* coalescence of two or more growth fronts into a single step has not been observed, which indicates the absence of impurities and imperfections in the crystals (Chalmers & Martins, 1952; Elbaum & Chalmers, 1955).

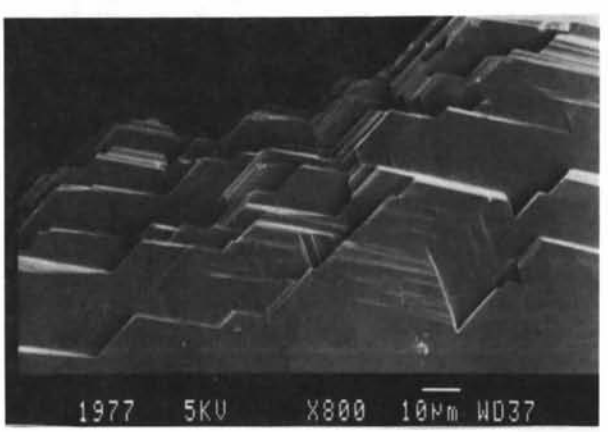

Fig. 7. Scanning electron micrograph of a dendrite showing zigzag growth steps.

The terminal points of the primary arms have a hexagonal shape, which conforms with the hexagonal symmetry of the PbI_2 crystals (Fig. 8). A closer look at the arms nearer the tip reveals also some curved steps (see Fig. 3). This implies that the rate of growth is relatively fast in the beginning. As the dendritic growth advances, the growth rate decreases. This is apparently the reason for the portion closer to the tip having 'better' primary arms than those farther from the tip.

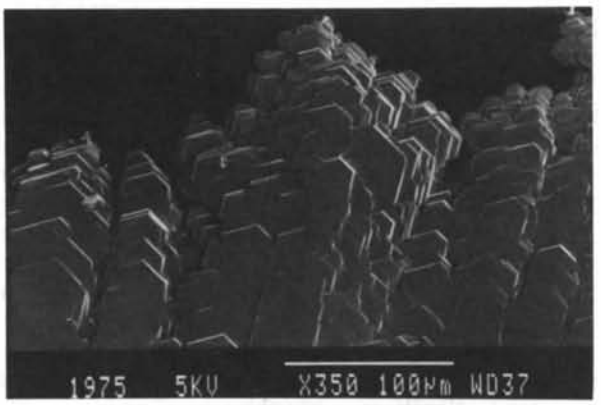

Fig. 8. Scanning electron micrograph of a dendrite showing primary arms; hexagonal terminal points are seen.

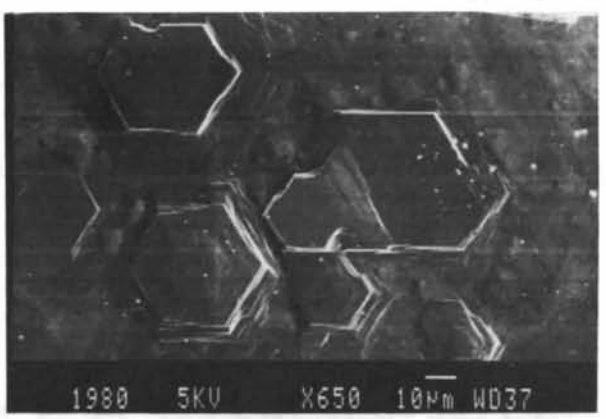

Fig. 9. Scanning electron micrograph of a dendrite showing hexagonal overgrowths on its surface.

Some hexagonal overgrowths are seen on the plane portion of the dendrite, shown in Fig. 3, a magnified view of which is shown in Fig. 9. Such overgrowths were not frequently observed. The hexagons are almost regular in shape. Sometimes the neighbouring hexagons coalesce as seen at two places in Fig. 9. The existence of such hexagonal overgrowth and the growth features seen in Figs. 7 and 8 are clearly indicative of a two-dimensional nucleation mechanism of crystal growth. Figs. 7 and 8 also indicate layer-by-layer growth. However, no spiral has been observed in any of the PbI_2 dendrites.

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