Five New Polytypes and Polytypic Change in PbI₂

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Abstract

Five new PbI₂ polytypes, 8H(1232), 10H(11121112), 10H(112222), 22H[11(22)], and 30R[11131313], were determined by the X-ray diffraction method. It was found on polytypic change that (a) the 2H polytype is changed into various polytypes on heating at 130°C and most of these further change to 12R[13] on heating at 260°C; (b) the polytypes 4H, faulted 4H, 14H, 22H, 26H and 30R with layer structures similar to the 12R[13] are fairly stable at high temperatures; (c) the 2H–30R[111313] transformation occurs reversibly.

Introduction

Layer stacking sequences in PbI₂ polytypes have been determined so far for the following eleven structures: 2H(11) (Terpstra & Westenbrink, 1926), 4H(22), 6H(1122) and 12R[13]* (Mitchell, 1959), 10H(11111122), 14H(1122) and 20H(11121112) (Agrawal, Chadha & Trigunayat, 1970), 24H(1112112112) (Mahesh & Trigunayat, 1976), 18R[1113] and 18R[1212] (Mahesh & Trigunayat, 1976) and 26H and 30R with layer structures similar to the 12R[13] (Chadha, 1976). It has been reported that the common polytypes of PbI₂ at low and high temperatures are 2H and 12R[13], respectively, and that the 2H–12R transformation occurs reversibly (Minagawa, 1975). In the present X-ray diffraction study, the layer sequences of five new polytypes were determined and various kinds of polytypic change by heating were found.

Five new polytypes

Hanoka & Vand (1968) found the polytypes 8H, 10H₁, 10H₂ and 30R in as-grown crystals. We determined the layer sequences of these polytypes and of a 22H polytype. The 10H₂ polytype was found in an as-grown crystal grown in gel. Five 8H, four 10H₁, two 22H, three 30R and two faulted 30R crystals were obtained by heating as-grown 2H crystals at 130°C for periods from one day to one month. Because Zhdanov symbols of the eleven polytypes described in the preceding section consist of the Zhdanov numbers 1, 2 and 3, the present five polytypes are assumed to keep this rule.

For PbI₂ polytypes, a Zhdanov symbol indicates only the stacking sequence of I layers. In this paper, Pb layers are inserted between the (2n – 1)th I layer (n a positive integer) and the 2nth in the layer sequence indicated by the Zhdanov symbol; therefore, [13], for example, represents a 12R polytype which is different from [31].

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The intensities were estimated visually with a scale of nine grades, e.g. 12/4c 2, since observed 22H reflexions are remarkably intense at and in the neighbourhood of the 4H reflexion positions; then there are 38 possible layer sequences for the 22H polytype. Calculated intensities for these five polytypes are assumed to keep this rule.

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Table 1. Comparison of the observed and calculated h0l intensities of the 8H, 10H₁, 10H₂ and 30R polytypes

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layer sequences were compared with observed ones, which were estimated visually from zero-layer Weissenberg photographs about the b axis, taken with Cu Kα radiation. The observed intensities agree with the calculated ones for the following layer sequences, \(8H(1232)\) with space group \(P3m1, a = a_0\) and \(c = 4c_0\), \(10H_{11112112}\) with \(P3m1, a = a_0\) and \(c = 5c_0\), \(10H_{112222}\) with \(P3m1, a = a_0\) and \(c = 5c_0\), \(22H_{1122(22)3}\) with \(P3m1, a = a_0\) and \(c = 11c_0\), \(30R_{[11131313]}\) with \(R3m, a = a_0\) and \(c = 15c_0\) (in hexagonal axes), where \(a_0 = 4.557\) and \(c_0 = 6.979\) Å (Swanson, Gilfrich & Ugrinic, 1955), the lattice constants of type 2H. Comparison of the observed and calculated intensities is given in Table 1. Observed intensities of the faulted 30R polytypes are in fair agreement with those of the 30R, but the reflexions are definitely shifted from the 30R reflexion positions.

### Polytypic change on heating

Many as-grown 2H crystals were heated at 130°C and atmospheric pressure for periods from one day to one month and quenched to room temperature; then their polytypic change was investigated by the Weissenberg photographs. Table 2 gives the frequency of occurrence of polytypes obtained. Of the polytypes given in Table 2, the following were changed into the 12R\([13]_3\) by heating at 260°C for one day: about a quarter of the 4H crystals plus faulted 4H, all 6H and 10H, three 14H, four 18R\([1113]\), of which three were found in as-grown crystals), two faulted 30R and all the hexagonal polytypes with periods beyond 26H.† All the resulting 12R crystals were confirmed to change back into the 2H polytype after being left at room temperature for one to six months (Minagawa, 1975). On the other hand, three quarters of the 4H crystals plus faulted 4H, two 14H, four 22H including two 22H\([11(22)5]\) and three 30R remained unchanged after being heated several times at 260°C or higher.

The remaining three 22H polytypes whose diffraction intensities were identical to one another (say 22H\(_{a}\) and the 26H (say 26H\(_{a}\)) were changed into 22H\(_{b}\) and 26H\(_{b}\), respectively, on heating at 260°C. As compared with the 22H\(_{a}\) and 26H\(_{a}\) polytypes, 22H\(_{b}\) and 26H\(_{b}\) resemble 4H closely in layer sequence; this was found from the fact that the 22H\(_{b}\)(26H\(_{b}\)) reflexions at and near the 4H reflexion positions are much stronger than the corresponding 22H\(_{d}\)(26H\(_{d}\)) reflexions. A similar experimental observation revealed that the two 14H crystals remaining unchanged on heating resemble the 4H type closely in layer sequence, unlike the three 14H changed into 12R. However, we failed in determining the Zhdanov symbols of the 14H, 22H\(_{a,b}\) and 26H\(_{a,b}\) polytypes.

The three 30R\([111313]\) crystals changed into the 2H polytype after being left at room temperature for half a month (Fig. 1a). The resulting three 2H crystals were changed back into the 30R polytype by heating at 130°C for one day (Fig. 1b). The 2H–30R transformation was repeatedly observed for the three crystals.

### Discussion

The 2H polytype is changed into various polytypes on heating at 130°C and most of these change further to the 12R\([13]_3\) on heating at 260°C. These facts indicate that both 2H and 12R polytypes are unstable in the

![Fig. 1. The 2H–30R reversible transformation. The 10l rows on Weissenberg photographs are compared. The index l refers to the c axial length of the 2H polytype. (a) 30R → 2H. (b) 2H → 30R; all spots except 2H are 30R.](image)
vicinity of 130°C and that 12R is the most stable polytype at high temperatures (Minagawa, 1975). The polytypes 4H, faulted 4H, 14H, 22H, 26H and 30R are fairly stable at high temperatures. This seems to be because their layer sequences are similar to that of 12R; the 12R consists of three unit cells of 4H and the layer sequences of the 14H, 22H and 26H are similar to the 4H. The faulted 30R→12R polytypic change is understood as follows; faulted layers in the faulted 30R polytype easily slip on heating and the slip helps to begin the polytypic change.

Hanoka & Vand (1968) proposed a growth mechanism of a 3nR polytype on an nH, by which a 3nR should coexist with the nH whose c axial length is one-third of that of the 3nR. Of the rhombohedral polytypes given in Table 2, all the faulted 12R coexist with the 4H, the 18R with the 6H and one 30R with a 10H whose layer sequence could not be determined. This fact indicates that the growth mechanism is applicable to 3nR crystals generated by polytypic change in the solid state. In the present case, furthermore, 12R \((AB) (AC) (BC) (BA) (CA) (CB)\) and 18R \((AB) (AC) (BC) (BA) (CA) (CB)\) can be generated from 4H \((AB)(AC)\) and 6H \((AB)(AB)(AC)\) respectively, by the slips \(A \rightarrow B \rightarrow C \rightarrow A\) and \(A \rightarrow C \rightarrow B \rightarrow A\) of the nH unit cell.

References