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Rietveld X-ray powder analysis of InBi crystalline structure at low temperatures

Ryszard Kubiak and Jan Janczak
W. Trzebiatowski Institute for Low Temperature and Structure Research, Polish Academy of Science, PO Box 937,50-950 Wrocław (Poland)

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Abstract

The dependence of the InBi crystalline structure on temperature (between 300 and 15 K) has been refined by the Rietveld method from X-ray powder diffraction data. The ranges of the lattice parameters (a and c) and the free parameter of the Bi atom (z) in the above temperature range are 5.0101(3)–4.9589(3) Å, 4.7824(3)–4.8396(3) Å and 0.3993(7)–0.3918(7) respectively.

1. Introduction

It was shown by Binnie [1] that InBi crystallizes in the space group $P4/nmm$ with the atoms at specific positions: In at $(0, 0, 0)$ and Bi at $(0, \frac{1}{2}, z)$. The dependences of the cell parameters [2, 3] and the z parameter of the bismuth atom [3] on temperature were studied in InBi single crystals. However, these examinations were performed only at temperatures above nitrogen boiling point.

In this paper we examined the InBi crystalline structure by X-ray powder diffractometry down to 15 K.

TABLE 1. Details of Rietveld refinement for InBi

2Θ range	20.00°–80.00°
Step scan size	0.02°
Number of points	3501
Profile function	Pearson VII
Background correction	Polynominal function
Number of refined parameters	13
Number of reflections	40
Full width at half-maximum (H) function	$H^2=(U\tan^2\Theta+V\tan\Theta+W)$
Space group	$P4/nmm$
Z	2

TABLE 2. Lattice parameters and z parameter of Bi atom *vs.* temperature

Temperature (K)	a (Å)	c (Å)	z (Bi)
300	5.0101(3)	4.7824(3)	0.3993(7)
200	4.9846(3)	4.8116(3)	0.3969(7)
100	4.9643(3)	4.8324(3)	0.3940(7)
50	4.9590(3)	4.8365(3)	0.3923(7)
15	4.9589(3)	4.8396(3)	0.3918(7)

2. Experimental details

The InBi compound was synthesized from 99.999% pure In and Bi. The InBi ingot was converted into powder in a mortar and then annealed at 350 K for a few days. The powder sample prepared in this way was characterized on a Siemens D-5000 powder diffractometer equipped with a helium low temperature attachment. The X-ray diffraction diagrams were collected for several temperature points (Bragg–Brentano

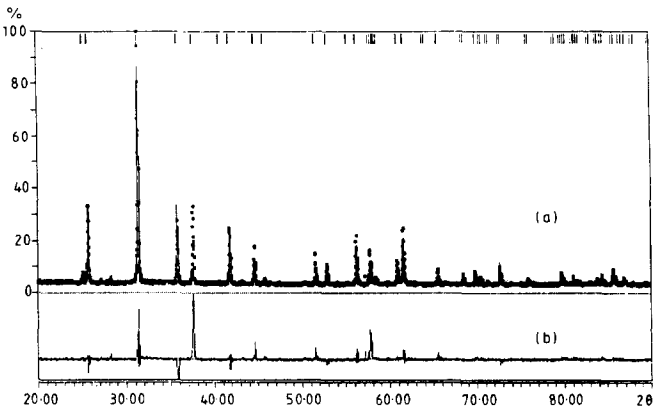

Fig. 1. Results of Rietveld refinement performed on sample of InBi: (a) measured and calculated diagram; (b) differential diagram and peak positions obtained at 15 K.

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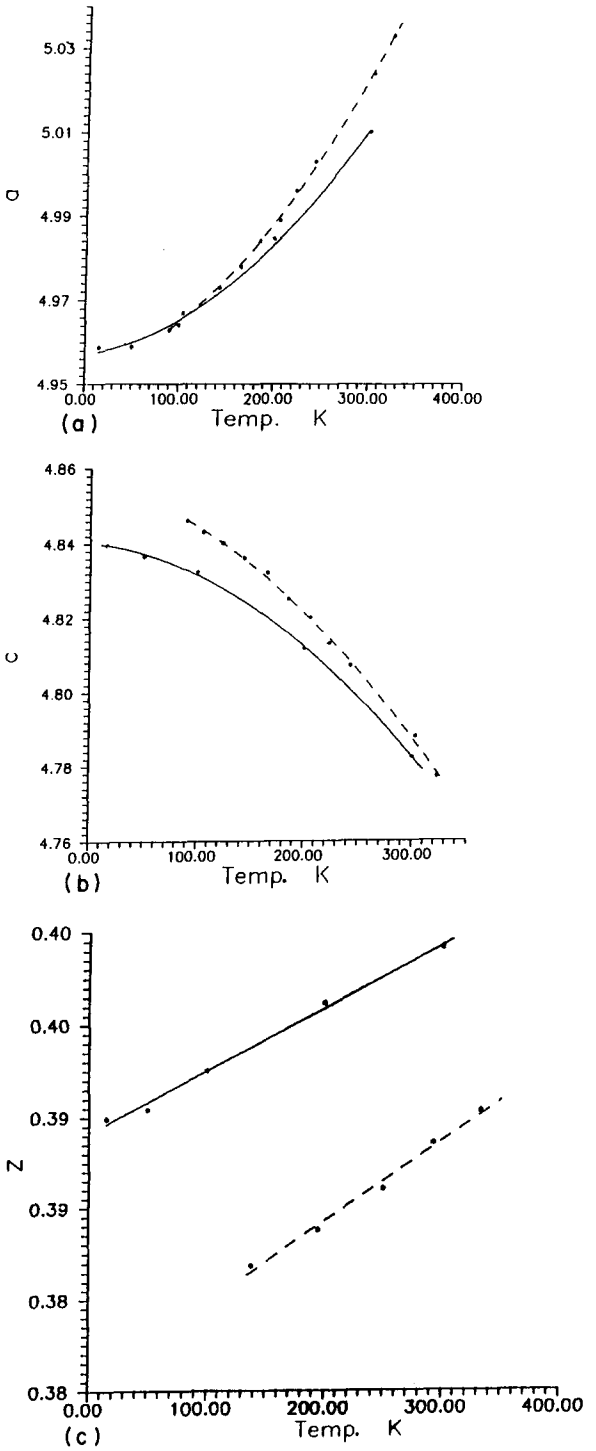

Fig. 2. Cell parameters (a, c) and free parameter of Bi atom (z) *vs.* temperature: (a) a; (b) c; (c) z.

geometry, Θ–Θ scan, Cu Kα radiation). The details of the refinement by the Rietveld method, performed with the DBWS-9006PC programme [4], are collected in Tables 1 and 2.

The mean R_p, R_{wp}, R_e and S factors obtained with the Rietveld refinement for InBi at the temperature points of Table 2 are equal to 0.090, 0.139, 0.056 and 2.54 respectively. The factors are defined as $R_p = \Sigma|y_{obs} - y_{cal}|/\Sigma y_{obs}$, $R_{wp} = [\Sigma w(y_{obs} - y_{cal})^2/wy_{obs}^2]^{1/2}$, $R_e = [(N-P)/\Sigma wy_{obs}^2]^{1/2}$, where N is the number of observations, P is the number of parameters refined and $w = 1/\sigma^2$ denotes the weights associated with y_{obs}, and S is the "goodness of fit", *i.e.* the ratio R_{wp}/R_e.

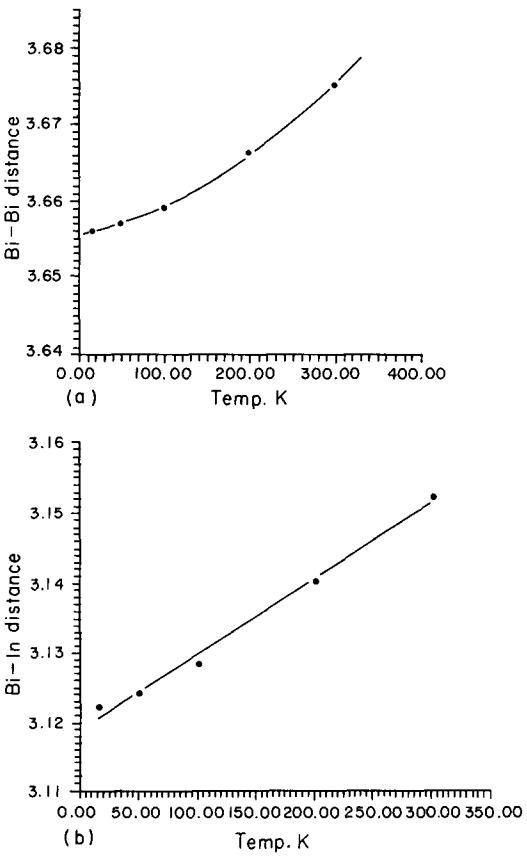

Fig. 3. Dependence of In–Bi and Bi–Bi distances on temperature.

3. Results and discussion

One of the experimental and theoretical X-ray powder diffraction diagrams for InBi is shown in Fig. 1. The calculated values of the cell parameters and the z parameter of the Bi atom *vs.* temperature are presented in Fig. 2. For comparison the literature data from single crystals (dashed curves) are also included in this figure. As can be seen from Fig. 2, the change in the parameters with temperature obtained from powder and single-crystal X-ray methods shows the same trend, but the corresponding curves do not coincide. This is undoubtedly caused by the different systematic errors in the two methods.

The Rietveld analysis performed on diagrams taken for InBi showed the greatest discrepancies for the (001)-type reflections. However, it is known that InBi possesses a marked cleavage plane normal to the c axis [1] and

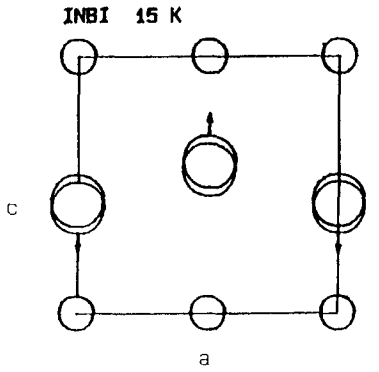

Fig. 4. Schematic diagram of relative shifts of unit cell parameters and z of Bi atom *vs.* temperature.

therefore we were not able to prepare a texture-free sample.

Taking into account that the two sets of data agree in trend, we calculated the changes in interatomic distances from our powder data. The In–Bi and Bi–Bi distances *vs.* temperature are shown in Fig. 3. The In–In distance of course changes in the same manner as the cell parameter a.

From these data it may be seen that the rate of shortening of the In–In and Bi–Bi distances diminishes with decreasing temperature. The In–Bi distances, however, shortened relatively more and practically linearly. The relative shifts of the cell parameters a and c and the parameter z of the Bi atom *vs.* temperature are shown schematically in Fig. 4.

Generally, it may also be concluded that the chemical character of the InBi compound changes and InBi becomes less metallic with decreasing temperature.

References

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