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Crystallographic study of the intermediate compounds SbZn, Sb_3Zn_4 and Sb_2Zn_3

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Abstract

The processes of development of semiconductor ceramics made up of bismuth, antimony and zinc often require during their preparation to know the nature of the involved phases. For that, it is always essential to refer to the diagrams of balance between phases of the binary systems or ternary. We presented in this work the study by X-rays diffraction relating to the intermediate compounds SbZn, Sb_3Zn_4 and Sb_2Zn_3. The analysis by X-rays is often useful to give supplement the results of the other experimental methods.

Keywords: X-rays; SbZn; Sb_3Zn_4; Sb_2Zn_3

1. Introduction

Some alloys of bismuth, antimony and zinc are semiconductor ceramics precursors. To fix a protocol of their preparation, it is necessary to have a thorough knowledge of their phase diagram. After a first study concerning the Bi–Zn system [1,2] and the study of two isothermal cuts in the Bi–Sb–Zn system [2] the experimental study of the Sb–Zn system has been undertaken because of the very controversy results found in the bibliography [3,4]. In the Sb–Zn system, appear three intermediate phases SbZn, Sb_3Zn_4 and Sb_2Zn_3. These compounds were characterized by means of the X-rays diffraction on powder.

2. Bibliographical analysis

The study of the phase diagram of the Sb–Zn system has been undertaken by many authors [5–18]. Their results are often very unmatched. The experimental study that we carried out made it possible to highlight three compounds.

The SbZn compound is stoechiometric, it breaks up at the temperature 544 °C according to the peritectic reaction: $SbZn \leftrightarrow Liq. + Sb_3Zn_4(\beta)$.

The Sb_3Zn_4 compound is of congruent fusion at the temperature 566 °C and exists in two allotropic forms β and γ.

The Sb_2Zn_3 compound, is also of congruent fusion at the temperature 568 °C and exists in two forms η and ζ. The latter breaks up at about 360 °C according to a reaction of the form: $3Sb_2Zn_3\ (\zeta) \leftrightarrow 2Sb_3Zn_4(\beta) + Zn$. The reverse reaction occurs at about 407 °C.

3. Experimental procedure and used materials

The identification of phases by X-rays diffraction has been carried PHILLIPS PW 1877 Version 3.5 diffractometer. For the high temperature tests, we have used a SIEMENS apparatus. The samples are reduced to a fine powder (<250 μm). This powder is then put on a glass plate. To avoid the risks of oxidation in the ambient air, a collodion drop is put on the surface. The indexing of the reflexions has been carried out starting from the inter-reticular distances from the X-rays diffraction diagram the refinement of the lattice parameters has been carried out by the least square method. Zinc is a Carlo Erba product containing less than 0.08% of impurities. Antimony is an Aldrich production of a content of 99.8%.

4. Results and discussion

The alloys to be analyzed by X-rays diffraction are recovered from the samples having undergone a calorimetric analysis in order to build the diagram phases of the Sb–Zn system. We separately present the results obtained for each compound.

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Table 1
Analysis results by X-rays diffraction of SbZn

2θ	I/I_0	d Measured
24.94	34.53	3.5702
25.96	58.27	3.4322
28.44	100.00	3.1383
29.04	94.24	3.0748
30.72	11.51	2.9103
32.76	64.75	2.7336
34.86	18.71	2.5736
36.24	20.86	2.4787
38.54	17.99	2.3359
43.04	15.83	2.1015
43.80	72.66	2.0668
45.82	37.41	1.9803
50.34	23.02	1.8126
50.58	24.46	1.8045
63.74	11.51	1.4601
63.88	25.18	1.4572
65.56	17.99	1.4239

4.1. SbZn compound

In Table 1, we have reported the numerical results of the analysis by X-rays diffraction of about the SbZn compound. This last has been already studied [12] and our results are in good agreement with those of the bibliography, we think that useless to reindex this compound.

4.2. Sb_3Zn_4 compound

In Table 2, we recomputed the inter-reticular distances indexed in the orthorhombic system and which are concordant with those of Psarev and Dobryden [12]. The latter indexed it in the same network and obtain the following parameters: $a = 7.981$ Å, $b = 7.495$ Å, $c = 10.72$ Å. In Fig. 1 we illustrated the X-rays of diffraction diagram of Sb_3Zn_4.

4.3. Sb_2Zn_3 compound

It has been not possible to us to obtain for this compound the X-rays diffraction diagram described by Dobryden and Psarev [12] or Lapkina et al. [16] even under exactly the same operating conditions. The former study the diagram, after water quenching

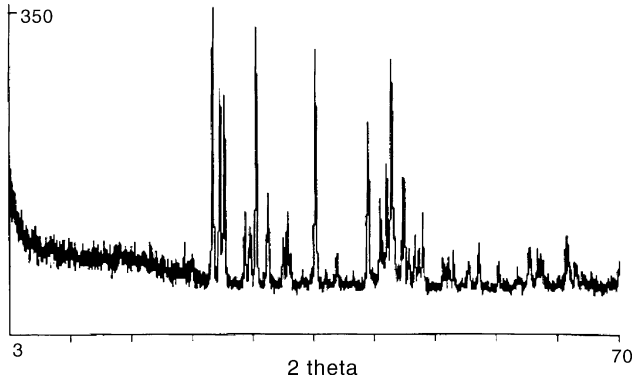

Fig. 1. X-rays diffraction diagram of Sb_3Zn_4.

Table 2
Indexation in the orthorhombic system Sb_3Zn_4

$h\,k\,l$	d Measured	d Calculated	I/I_0
0 0 1	10.9286	11.3158	18.83
0 1 0	7.2605	7.3453	18.39
2 0 1	3.8453	3.7841	14.35
0 0 3	3.8453	3.7719	14.35
1 1 2	3.8453	3.9139	14.35
0 2 1	3.5079	3.4933	98.65
2 1 0	3.5790	3.5232	98.65
1 0 3	3.4076	3.4141	80.27
0 1 3	3.3448	3.3554	72.20
1 2 0	3.3448	3.3399	72.20
2 1 1	3.3448	3.3639	72.20
0 2 2	3.0883	3.0805	29.15
1 1 3	3.0883	3.0960	29.15
2 1 2	2.9641	2.9908	100.0
0 0 4	2.8444	2.8289	37.22
2 2 0	2.7008	2.7100	19.28
1 0 4	2.6664	2.6682	29.60
3 0 0	2.6664	2.6768	29.60
2 1 3	2.5488	2.5747	4.93
3 1 0	2.5488	2.5150	4.93
0 3 0	2.4481	2.4484	91.93
2 2 2	2.4481	2.4441	91.93
3 1 1	2.4481	2.4551	91.93
1 3 1	2.3020	2.2934	13.00
3 1 2	2.3020	2.2982	13.00
3 2 1	2.1256	2.1247	64.57
1 1 5	2.0727	2.0884	8.97
2 3 0	2.0727	2.0904	8.97
2 3 1	2.0619	2.0557	32.29
3 2 2	2.0312	2.0206	47.53
4 0 0	2.0098	2.0076	89.69
2 2 4	1.9549	1.9570	44.39
2 3 2	1.9549	1.9609	44.39
0 2 5	1.9321	1.9267	13.45
4 1 0	1.9321	1.9366	13.45
2 1 5	1.9069	1.9042	17.94
0 0 6	1.8905	1.8860	15.70
4 0 2	1.8905	1.8920	15.70
1 2 5	1.8744	1.8735	23.77
3 1 4	1.8744	1.8797	23.77
3 2 3	1.8744	1.8765	23.77
1 4 0	1.7969	1.7901	07.62
3 3 1	1.7493	1.7841	10.76
1 1 6	1.7493	1.7812	10.76
4 2 0	1.7608	1.7616	13.45
2 0 6	1.7107	1.7070	10.76
0 2 6	1.6783	1.6777	15.70
2 3 4	1.6783	1.6812	15.70
3 1 5	1.6783	1.6823	15.70
4 2 2	1.6783	1.6820	15.70
1 4 3	1.6179	1.6172	08.97
3 2 5	1.5667	1.5638	7.17
0 4 4	1.5383	1.5403	13.90
4 3 1	1.5383	1.5381	13.90
5 1 2	1.5155	1.5120	15.25
3 4 0	1.5155	1.5143	15.25
5 1 3	1.4501	1.4487	16.59
1 5 1	1.4307	1.4334	11.66
2 4 5	1.3439	1.3437	12.11
2 5 2	1.3439	1.3403	12.11
4 4 1	1.3439	1.3454	12.11

$a = (8.03 \pm 0.01)$ Å; $b = (7.34 \pm 0.01)$ Å; $c = (11.31 \pm 0.02)$ Å.

of alloy of Sb_2Zn_3 composition, from the temperature 420 °C. The latter operate differently, they maintain the alloy at 440 °C for 350 h and soak it. All the tests we carried out lead to the same result. The alloy Sb_2Zn_3 always break up into a mixture of Zn and Sb_3Zn_4. We reproduced (Fig. 2) an example of the X-rays diffraction diagram for Sb_2Zn_3 alloy molten and then slowly cooled.

In a second series of experiences, we tried to show the formation of the Sb_2Zn_3 phase by gradually reheating this compound from 100 to 480 °C with 10 °C as a step and plot for every step the X-rays diagram. The operations are carried out under nitrogen sweeping. As the temperature increases, Sb_3Zn_4 diagram disappears and that of the zincite ZnO appears. It seems that the circulating gas contains oxygen traces involving a phenomenon of oxidation starting from the temperatures of phase shift. In order to compare the diagram of this alloy with that of Sb_3Zn_4, we recomputed in the orthorhombic system the inter-reticular distances. The results are deferred in Table 3.One obtains most of the computed lines of the compound Sb_3Zn_4.

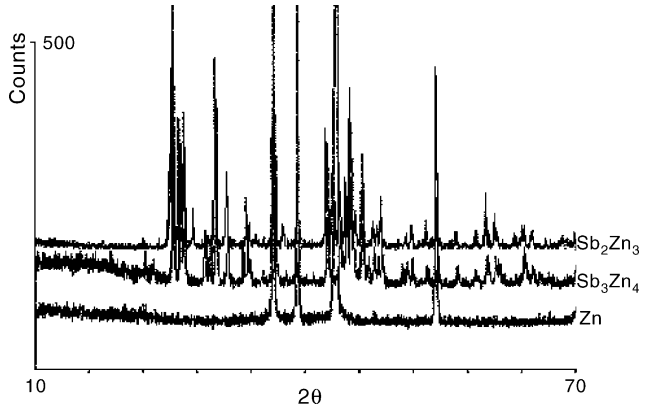

Fig. 2. X-rays diffraction diagram of Sb_2Zn_3.

Table 3
Indexation in the orthorhombic system Sb_2Zn_3

h k l	*d* Measured	*d* Calculated	I/I_0
0 0 1	11.3050	11.3217	12.24
0 2 1	3.5079	3.4910	100.0
2 1 0	3.5079	3.5236	100.0
1 0 3	3.4076	3.4158	50.53
0 1 3	3.3448	3.3562	45.10
1 2 0	3.3448	3.3378	45.10
2 1 1	3.3448	3.3644	45.10
0 2 2	3.0511	3.0791	5.94
2 1 2	2.9641	2.9914	59.79
0 0 4	2.8444	2.8304	30.07
1 0 4	2.6664	2.6696	17.48
3 0 0	2.6664	2.6779	17.48
0 3 0	2.4481	2.4463	76.92
2 2 2	2.4481	2.4438	76.92
3 1 1	2.4481	2.4558	76.92
1 3 1	2.3009	2.2918	13.64
3 1 2	2.3009	2.2989	13.64
3 2 1	2.1265	2.1247	40.91
1 1 5	2.0836	2.0892	13.99
2 3 0	2.0836	2.0893	13.99
2 3 1	2.0628	2.0546	20.63
3 2 2	2.0312	2.0206	52.80
4 0 0	2.0106	2.0084	69.58
2 2 4	1.9541	1.9571	27.62
2 3 2	1.9541	1.9601	27.62
0 2 5	1.9206	1.9270	4.20
2 1 5	1.9069	1.9049	15.73
0 0 6	1.8913	1.8870	12.59
4 0 2	1.8913	1.8928	12.59
1 2 5	1.8759	1.8738	16.08
3 1 4	1.8759	1.8803	16.08
3 2 3	1.8759	1.8767	16.08
3 3 1	1.7819	1.7836	6.29
1 1 6	1.7859	1.7820	6.29
4 2 0	1.7608	1.7618	13.64
2 0 6	1.7107	1.7079	9.79
0 2 6	1.6800	1.6781	9.44
2 3 4	1.6800	1.6810	9.44
3 1 5	1.6800	1.6830	9.44
4 2 2	1.6800	1.6822	9.44
1 4 3	1.6190	1.6163	8.74
0 4 4	1.5397	1.5396	10.14
4 3 1	1.5397	1.5379	10.14
5 1 2	1.5151	1.5125	11.89
3 4 0	1.5151	1.5136	11.89
5 1 3	1.4473	1.4492	10.84
1 5 1	1.4303	1.4323	9.09

$a = (8.03 \pm 0.01)$ Å; $b = (7.34 \pm 0.01)$ Å; $c = (11.32 \pm 0.01)$ Å.

5. Conclusion

Following several experimental studies of the binary systems Bi–Zn and Sb–Zn and ternary systems Bi–Sb–Zn for the development of semiconductor ceramics, we were interested in the analyses by diffraction of X-rays in several fields of phases and for certain intermediaries. In this work, we present the analysis results by X-rays diffraction of obtained by studying the intermediate compounds SbZn, Sb_3Zn_4 and Sb_2Zn_3 existing in the diagram of balance between phases of the Sb–Zn binary system. Concerning the SbZn compound, our results agree perfectly with those of the literature. For the Sb_3Zn_4 compound, we indexed it in the orthorhombic system and its definite lattice parameters. As for Sb_2Zn_3, it was impossible to obtain a diffraction diagram specific to this compound since it does not exist at ambient temperature. It always breaks up into Zn and Sb_3Zn_4.

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