

NEW CONTRIBUTION IN THE STUDY OF THE Bi_2Te_3 - Bi_2Se_3 SYSTEM.

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SUMMARY

Through X-ray, D.T.A. and microstructural analysis, phase interactions in the Bi_2Te_3 - Bi_2Se_3 section were investigated and the phase diagram was described. The result was not a simple solid solution region as had been previously supposed. A more complex subsolidus pattern was discovered with two terminal solid solutions α and α' and a zone of demixion.

An intermediate phase $\text{Bi}_2\text{Te}_2\text{Se}$ was confirmed, its properties and conditions of existence described in the new context.

INTRODUCTION

The materials used in the thermoelectric conversion of energy -particularly the N-type elements of the thermoelectric modules- are polyconstituent alloys based on bismuth, antimony, tellurium and selenium. The physical characteristics of the materials and their optimisation depend on the exact nature of the equilibrium diagram.

Discrepancies discovered between D.T.A. measurements and earlier results, revealed a need for further explanation and deeper investigations.

The new approach to the Bi_2Te_3 - Bi_2Se_3 system proposed in this paper reveals the presence of an intermediate compound $\text{Bi}_2\text{Te}_2\text{Se}$ and appears to be more exact than previous methods.

EXPERIMENTS

Sample preparation

The bismuth, tellurium and selenium compounds were mixed in various proportions and heated in quartz ampoules under a vacuum of 10^{-4} torr. The heat treatment adopted for each composition was melting and homogenisation of the mixtures followed by slow cooling and annealing at a temperature below that of the transition temperature observed in DTA analysis. Since it was discovered that equilibria are established extremely slowly, one to two month annealing treatments are required.

Experimental techniques

The thermal analysis was carried out with an instrument constructed in our own laboratory (ref. 1). The range sensitivity used in this work was 0-0.25 mV.

High temperature X-ray diffraction apparatus was used as a function of temperature and composition in order to study solid state equilibria.

Dilatometric analyses were performed on a small compacted powder bar by means of an Adamel apparatus.

The characterization of the alloys was performed through optical metallography, the chemical composition determined by using microprobe analysis apparatus.

STUDY OF THE PHASE DIAGRAM $\text{Bi}_2\text{Te}_3\text{-Bi}_2\text{Se}_3$

The cross section $\text{Bi}_2\text{Te}_3\text{-Bi}_2\text{Se}_3$ of the Bi-Te-Se phase diagram has been studied previously (refs. 2-3-4) (Fig. 1). Because of a discrepancy between our measurements and those previously reported, it was necessary to reinvestigate this phase diagram which was studied by D.T.A. during heating cycles and radiocrystallographic analysis of the alloys.

The temperatures corresponding to the accidents observed in DTA curves have been reported in Table 1. The phase diagram (Fig. 2) has been constructed using these same observations.

TABLE 1

Thermal effects in the DTA study of the $\text{Bi}_2\text{Te}_3 - \text{Bi}_2\text{Se}_3$ system.

Molar ratio in Bi_2Se_3	Invariant T/K	Solidus T/K	Liquidus T/K
0.0			858
0.05			855
0.10			858
0.20	862		897
0.30	863		911
* 0.333	863		915
0.35	861		919
0.40	864		924
0.50	865		935
0.60		870	946
0.70		879	955
0.80		896	965
0.90		909	973
1.00			981

* This composition corresponds to the $\text{Bi}_2\text{Te}_2\text{Se}$ formula.

This system is characterized by an invariant at (863 ± 2) K. Its Tammann diagram indicates a maximum molar composition of 22 mol % Bi_2Se_3 . Solubility limits of the α and α' phases were determined by analysing alloys quenched at a temperature

in the vicinity of the invariant and also by analysing samples obtained through directional solidification.

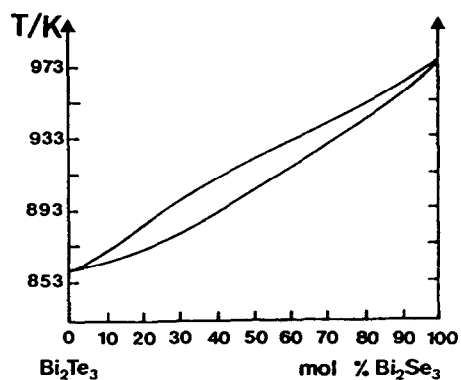


Fig. 1. Bi_2Te_3 - Bi_2Se_3 phase diagram by Mc Hugh et al.

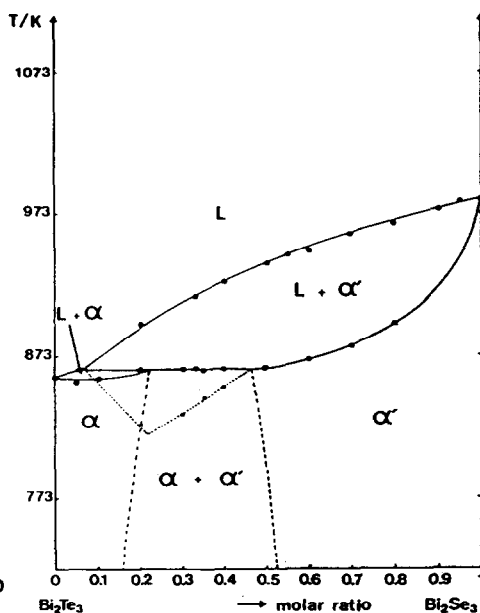


Fig. 2. Bi_2Te_3 - Bi_2Se_3 phase diagram.

Least square fitting of unit cell parameters in the whole composition range indicates the solubility limits as 22 and 48 mol % in Bi_2Se_3 for α and α' phases respectively (Table 2).

TABLE 2

Bi_2Te_3 - Bi_2Se_3 alloys : unit cell parameters.

Bi_2Se_3	0.0	0.1	*0.333	0.5	0.6	0.7	0.9	1.0
a(pm)	438.6	435.8	429.8	425.6	423.6	421.0	414.0	414.3
b(pm)	3049.7	3034.2	2977.4	2972.3	2956.1	2935.4	2886.1	2863.6

* This composition corresponds to the $\text{Bi}_2\text{Te}_2\text{Se}$ formula.

It was observed that the alloy corresponding to the $\text{Bi}_2\text{Te}_2\text{Se}$ formula demonstrates a particular characteristic in that its X-ray diffraction pattern corresponds to a well defined single phase.

Moreover, the $\text{Bi}(\text{Te}_{0.78}\text{Se}_{0.22})_3$ composition was confirmed by microprobe analysis on an ingot directionally solidified by means of the Bridgman method.

The solubility limits could not be determined at low temperatures, since it was extremely difficult to achieve thermal equilibrium. Solvus lines were drawn.

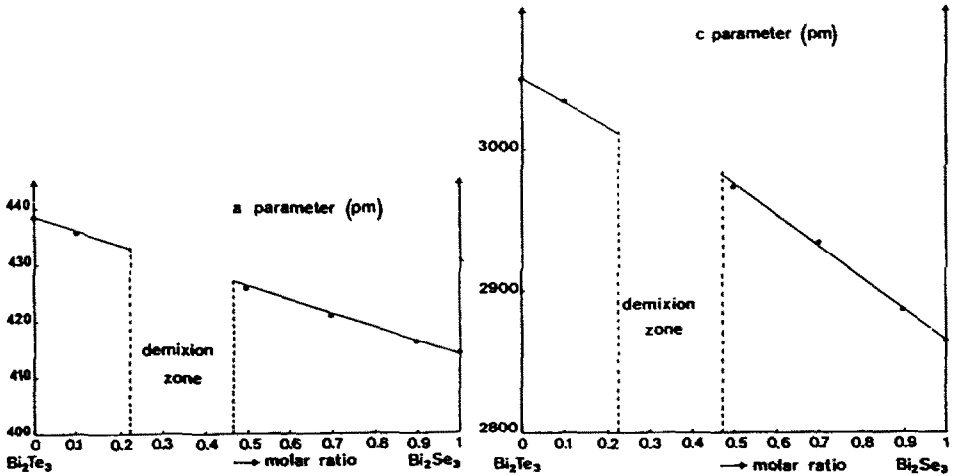


Fig. 3. Unit cell parameters in the Bi_2Te_3 - Bi_2Se_3 system.

In the $[3(\text{Bi}_2\text{Te}_3), \text{Bi}_2\text{Se}_3]$ alloy annealed for more than 15 days at 600 K, a solid state reaction took place, resulting in a $\text{Bi}_2\text{Te}_2\text{Se}$ phase different from the mixture of $\alpha + \alpha'$ generally observed for this composition.

The phase diagram presented here does not allow us to anticipate the existence of that intermediate phase, which is due to a very slow atomic rearrangement below the transformation temperature determined elsewhere (about 626 ± 2)K, a transformation first indicated by Bland et al. (ref. 5). This new phase was presented as an isomorph of the tetradymit $\text{Bi}_2\text{Te}_2\text{S}$. A previous report on the system Sb_2Te_3 - Sb_2Se_3 leads one to expect another ordered phase $\text{Bi}_2\text{Te}_2\text{Se}$ (ref. 6). However, no such phase resulted from our experiments.

PHYSICOCHEMICAL CHARACTERIZATION OF THE ALLOYS

As mentioned above, the refinements of solid solution unit cell parameters were made by recording the X-ray powder diagrams. These values are plotted as a function of molar fraction of Bi_2Se_3 (Fig. 3). As can be observed from this graph, the values decrease in proportion to the quantity of selenium introduced. Because of difficulties encountered in separating the lines due to the different phases on the X-ray diagrams,

it was impossible to refine the unit cell parameters for the composition lying between 22 and 48 moles % Bi_2Se_3 .

When studied in more detail, the new compound $\text{Bi}_2\text{Te}_2\text{Se}$ proved to have a rhombohedral structure and belong to the $R\bar{3}m$ space group.

Hexagonal unit cell parameters were calculated thusly :

$$a = 429.8 \text{ pm} \quad c = 2977.0 \text{ pm}.$$

The thermal behaviour of this material was studied by measuring electrical resistivity (using the Van der Pauw method) and by X-ray diffraction as a function of temperature (using a Guinier camera).

The temperature dependance of conductivity revealed a semiconduction behaviour, as expected. In addition, a change in the slope was observed between 583 and 658 K (Fig. 4). The study of diffractogram evolution with temperature also showed a modification around 630 K (Fig. 5).

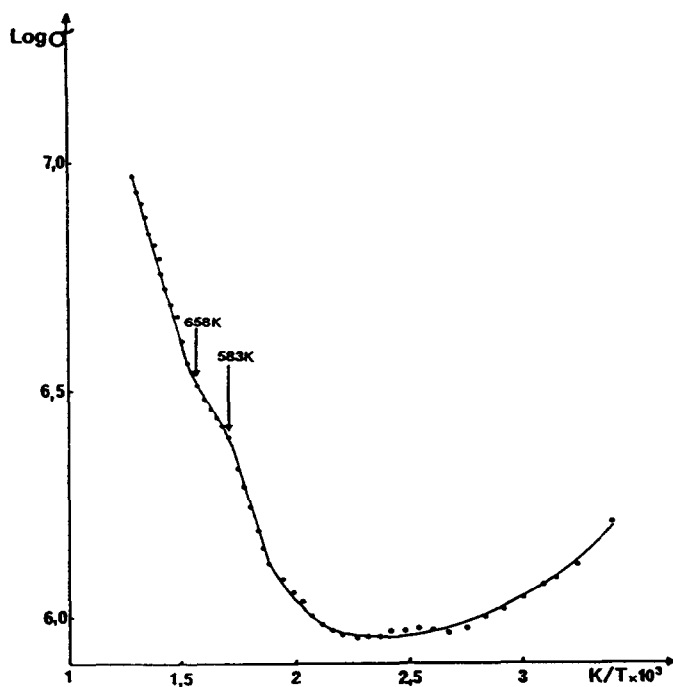


Fig. 4. $\text{Log } \sigma$ plot as a function of $1/T$.

The diffraction peaks of $\text{Bi}_2\text{Te}_2\text{Se}$ are conserved with slight modification in position up to this temperature, beyond which the peaks appear to be characteristic of α and α' . The electrical conductivity curve also indicates that the transformation in the same temperature range of (630 ± 2) K is conserved after cooling, indicating that the reaction $\text{Bi}_2\text{Te}_2\text{Se} + x\alpha + y\alpha'$ is not reversible.

The preceding was verified by several direct dilatometric tests carried out on the compacted powders, during which an anomaly in the variation of length was noted at the temperature of 630 K. In this case as well, the phenomena proved irreversible during cooling.

In the light of the observations made above, the following equilibria for different temperature ranges can be established :

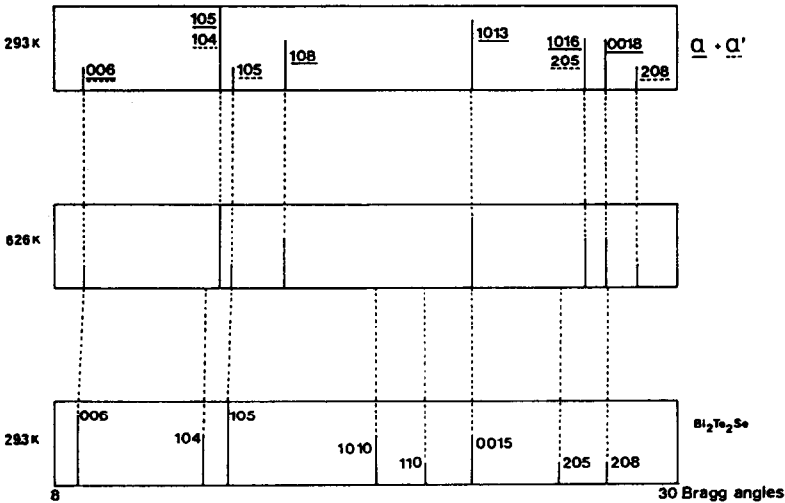
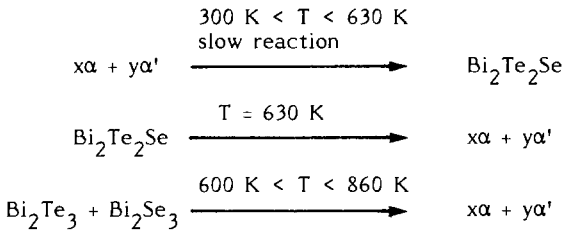


Fig. 5. Bi_2Te_3 - Bi_2Se_3 X-ray diffractograms as a function of temperature.

CONCLUSION

The system $\text{Bi}_2\text{Te}_3\text{-Bi}_2\text{Se}_3$ was studied and the system's characteristics were brought out. Two solid solutions formed from the constituents were revealed and the physical characteristics of the intermediate compound $\text{Bi}_2\text{Te}_2\text{Se}$ were studied.

The results of the present work are significantly different from those previously reported. In particular, the liquid-solid equilibrium differ on two points : the shape of solidus and the presence of the $\text{Bi}_2\text{Te}_2\text{Se}$ phase.

The conclusions reached should be of interest because they may affect the conception of thermoelectric materials fabricated with this system.

ACKNOWLEDGEMENT

This work has been supported by the "Direction des Recherches et Etudes Techniques" (contrat n°84.34.048.00.470.75.01).

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