Thermochimica Acta, 165 (1990) 93–101
Elsevier Science Publishers B.V., Amsterdam

REDETERMINATION OF THE PHASE EQUILIBRIA IN THE SYSTEM Tl_2Te–Ag_2Te

GERARD BRUN, MAHJOUB BOUBALI, JEAN-CLAUDE TEDENAC
and R.M. AYRAL

Laboratoire de Chimie des Matériaux Solides, Université de Montpellier II, Sciences et Techniques du Languedoc, Place E. Bataillon 34095 Montpellier Cedex 2 (France)

BERNARD LEGENDRE

Université de Paris Sud — Faculté de Pharmacie, Rue Jean Baptiste Clément, 92296 Chatenay-Malabry (France)

(Received 21 December 1989)

ABSTRACT

The Tl_2Te–Ag_2Te system phase equilibria have been redetermined by DTA, X-ray diffraction and the measurement of thermoelectric power. The existence of the phase Tl_2Te was first established and its crystallographic parameters were determined. At least four compounds are formed in the system. The crystallographic parameters of the congruently melting AgTlTe (483°C) and the incongruently melting $AgTl_3Te_2$ (382°C), $Ag_8Tl_2Te_5$ (440°C) Ag_5TlTe_3 (446°C) and Ag_9TlTe_5 (504°C) were determined. The 0–50 mol% Ag_2Te range of the system is non-quasi-binary and a narrow solid solution range around the AgTlTe composition gives a new insight into its dimorphic transformation.

INTRODUCTION

Interest in the thermoelectric properties of AgTlTe or its copper-substituted ($Ag_{1-x}Cu_xTlTe$) compounds [1,2] has lead us to define the boundaries of that phase as well as the equilibria conditions of all the other phases of the Tl_2Te–Ag_2Te binary system. For many years, the results of Babanly and Kuliev [3] for the Ag–Tl–Te ternary and of Abishov et al. [4] for the Tl_2Te–Ag_2Te binary proved to be adequate.

However, the continued controversy concerning the existence of Tl_2Te, recent results concerning the polymorphism of AgTlTe [5] and new compounds formed in the system [6] make it necessary to verify the existing data relating to the phase equilibria. The phase diagram of the system established by us differs significantly from those published previously. New precise definitions resulting from the crystallographic data have clarified the general understanding of the system and have corroborated our conclusions resulting from the DTA, DSC and also the thermoelectric power measurements.

EXPERIMENTAL

About forty compositions were prepared by fusing together the corresponding high purity elements (Te, 5N, Ventron; Ag, 5N Aldrich Chem.; Tl, 3N Aldrich Chem., refined by fusion and recrystallisation) in stoichiometric proportions in sealed quartz ampoules evacuated to 10^{-5} bar. The annealing temperatures were approximately 300 °C and the annealing times varied from 3 weeks to 1 month. After this thermal treatment, each sample was first characterised by X-ray diffractometry and studied by differential thermal analysis (in a home-made or a Netzsch apparatus) with a heating rate of 260 °C h^{-1}. A calorimetric analysis was then performed on a DSC (Setaram apparatus) with a heating rate of 30 °C h^{-1}. After grinding the annealed solidified melts and pressing the powder into a disc, the thermoelectric power measurements were made using an apparatus described elsewhere [7].

EVIDENCE FOR THE Tl_2Te PHASE IN THE Tl–Te SYSTEM

In spite of detailed information and proof concerning the existence of a solid or liquid Tl_2Te phase [8–11], this compound never appeared in the Tl–Te phase diagram until the results of Asadov et al. [12]. In most of the other reports [13–15], the composition corresponding to Tl_2Te (i.e. 33.3% Te in the Tl–Te system) constitutes at the very most the lower limit of the γ-solid-solution, the upper one corresponding to the compound Tl_5Te_3 (37.5% Te). In ref. 12, the compound Tl_2Te is perfectly defined with a congruent melting temperature of 425 °C. Considering the differences in the

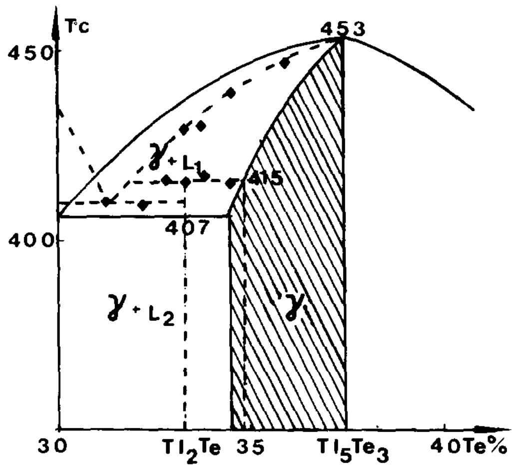

Fig. 1. Phase diagram for the Tl–Te system between 30 and 40 mol% Te. Dotted line = metastable equilibria.

phase diagrams published for the Tl–Te system, we studied the composition range 30–40% Te only and made the following conclusions (Fig. 1).

(1) The publications which ignore the existence of a Tl_2Te phase describe stable equilibria in that composition range. However, the homogeneity range of the γ-phase appears narrower (from 34.5 to 37.5% Te) and excludes the Tl_2Te composition. After two months of annealing at 350 ° C, a sample of Tl_2Te composition (33.3% Te) is composed of two phases (Tl + γ-phase).

(2) A metastable phase diagram equilibrium (dotted line on Fig. 1) exists with Tl_2Te as a distinct solid phase, melting incongruently at 415 ° C, which is obtained by melting and one week of annealing of the corresponding stoichiometric composition. It is perfectly characterised by X-ray crystallography.

(3) Addition of only 1% Ag_2Te to 99% Tl_2Te is enough to stabilise the structure in the solid state. No transformation is observed even after three months of annealing. A single crystal was isolated and the crystallographic parameters were determined. Tl_2Te crystallises in the triclinic system, $P\bar{1}$, with the lattice parameters: $a = 15.572$ Å; $b = 9.018$ Å; $c = 30.965$ Å; $\alpha = 90.88°$; $\beta = 80.87°$; and $\gamma = 89.65°$. The measured density of 8.38 g cm^{-3} corresponds to 40 formulae per unit cell.

DESCRIPTION OF THE Tl_2Te–Ag_2Te SYSTEM

The phase diagram (Fig. 2) was established from the thermal analysis and crystallographic results. For the molecular ratio of Tl_2Te/Ag_2Te close to unity, the melting temperature measured (483° C) is a maximum which corresponds to the congruence of the composition $Ag_{1.02}Tl_{0.98}Te$ (i.e. $Ag_{0.34}Tl_{0.326}Te_{0.33}$). A narrow solid solution range (from 50 to 51% Ag_2Te) is observed for silver-enriched AgTlTe compositions, in contrast to what was observed in a similar section of the ternary system [5]. The cell parameters do not vary very much in that range which coincides with a thermoelectric power maximum (Fig. 3). As has been reported [1,2,6], the compound undergoes a polymorphic transformation.

Two invariants are observed at the right and the left of the composition for temperatures of 447 and 400 ° C, with a two-phase region in the interval, as is shown in the detail in Fig. 2 and described in Table 1 (part II). This interpretation of the data is the result of a detailed investigation of this region and differs greatly from earlier and even recent results.

Besides AgTlTe, four more compounds are formed in the system, each melting incongruently: $AgTl_3Te_2$ (382° C), $Ag_8Tl_2Te_5$ (440 ° C), Ag_5TlTe_3 (446 ° C) and $AgTlTe_5$ (504 ° C) whose invariants are described in Table 1. The non-quasi-binary state of the first range, 0–50% Ag_2Te, is demonstrated by the formation of two three-phase domains and results from the incongruency of the compound Tl_2Te.

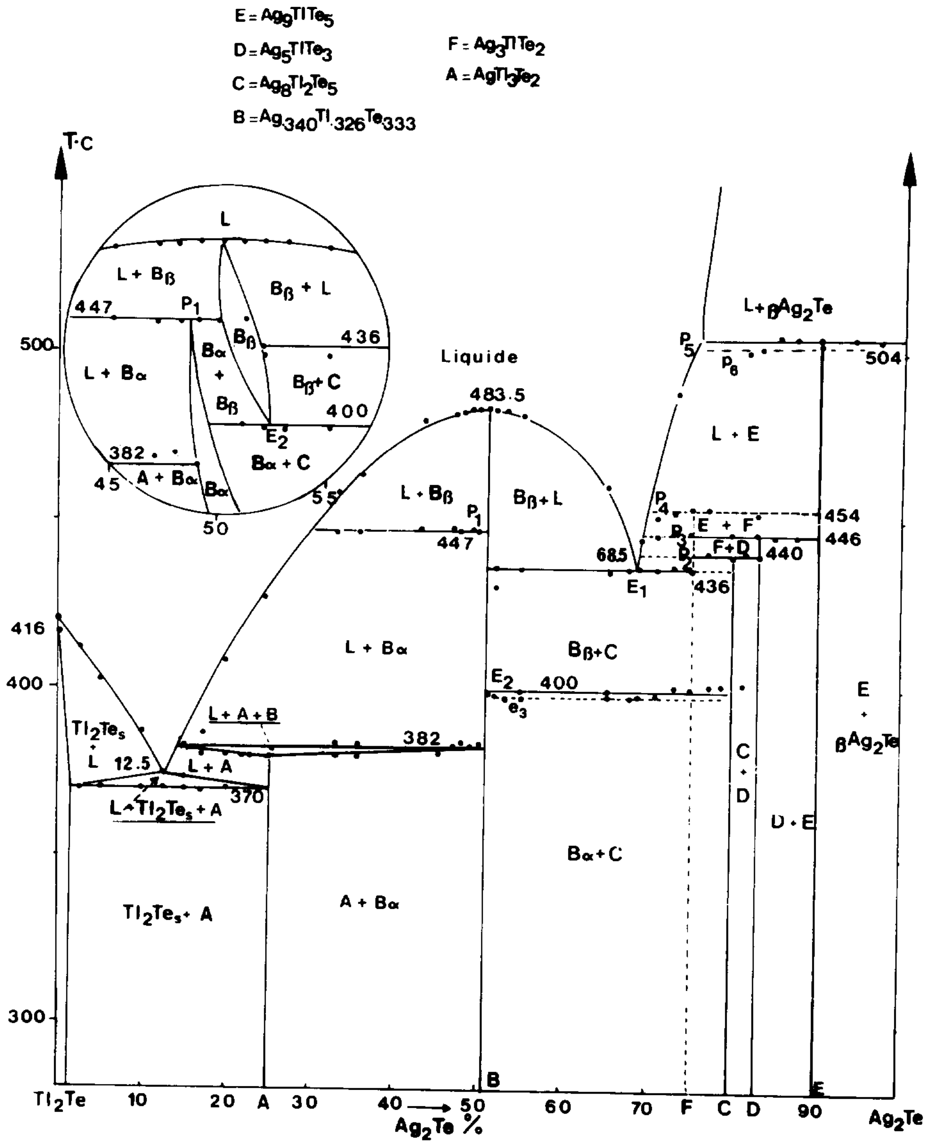

Fig. 2. Phase diagram for the Tl_2Te–Ag_2Te system.

The minimum temperature for the liquidus line is observed for the composition 12.5% Ag_2Te. A solid solution *s* (Tl_2Te*s*) for up to 1% Ag_2Te (at 370 °C) which is stable up to room temperature, is suggested by the maximum of the thermoelectric power (Fig. 3) and by observations of the peaks of the X-ray diffraction pattern.

The investigation of phase equilibria within the region of $Ag_2Te > 50\%$

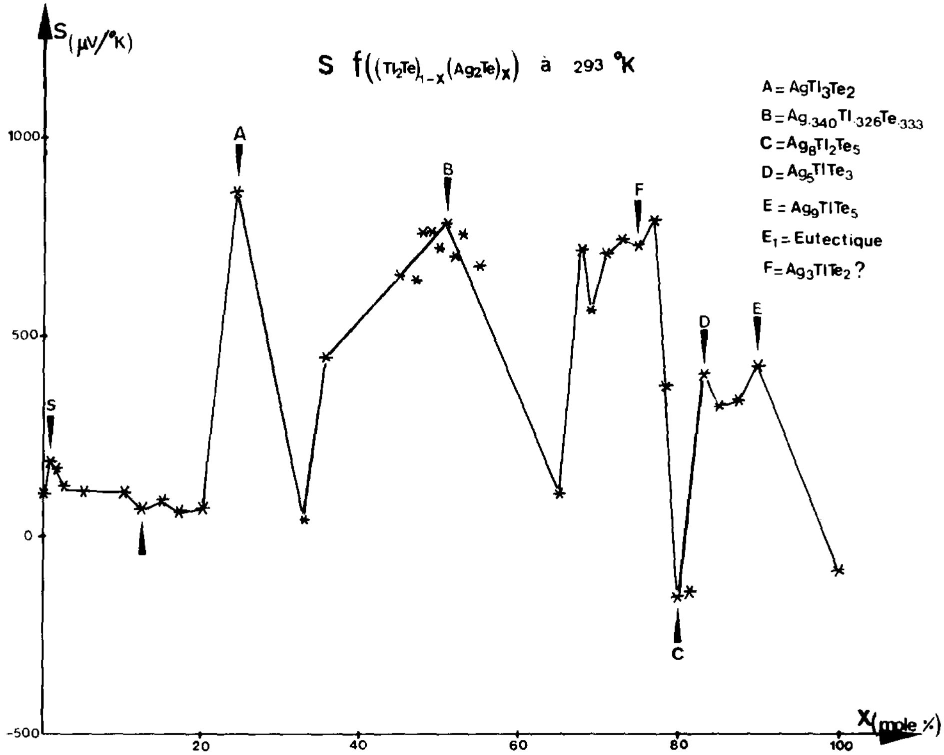

Fig. 3. Dependence of the thermoelectric power (*S*) on the composition of the solid samples at room temperature.

and the temperature range 400–450 °C presented the greatest difficulty, mainly due to the overlapping of the heat effects during the determination of the cooling curves. X-ray diffractometry of the samples can provide a clearer solution to the problems so long as the crystallographic parameters of the phases are known; this is the case for the phases $Ag_8Tl_2Te_5$ (C), Ag_5TlTe_3 (D) and Ag_9TlTe_5 (E) (Fig. 4). One important fact must be pointed out: the samples resulting from solid state reactions after two weeks of annealing the mixed powders at 300 °C (xAgTlTe + yAg + zTe) show X-ray patterns of better quality (good crystallinity) than samples melted first and then annealed (e.g. the patterns of samples that have undergone the successive heat effects close to 450%). The position of the invariant eutectic at 436 °C is easy to find from experimental points and by the Tammann triangle method. Because the invariants P_2 and P_3 correspond to the described phase equilibria (Table 1), the points remaining at around 454 °C have to be explained. The maximum heating effect at that temperature is observed for the composition 75% Ag_2Te (Ag_3TlTe_2, F). Keeping in mind that such a compound would have to be obtained by vacuum deposition [16] and its structure determined by electronic diffraction, and that a similar composi-

TABLE 1

Most essential data on the phase equilibria in the Tl_2Te–Ag_2Te system

---

I Non-quasi-binary range 0–50 mol% Ag_2Te

— Tl_2Te melting range (416–429 °C)

— a range of limited solid solution: 1 mol% Ag_2Te (Tl_2Te_s)

— a transformation at 382 °C of the 3 : 1 compound ($AgTl_3Te_2$) through a three-phase zone: liq. + $AgTl_3Te_2$ + α-AgTlTe (B)

— at 12.5 mol% Ag_2Te, a three-phase transformation (near 370 °C)
liq. $\leftrightarrows$ liq. + $AgTl_3Te_2$ + Tl_2Te_s $\leftrightarrows$ $AgTl_3Te_2$ + Tl_2Te_s

II Solid solution 50–51 mol% Ag_2Te

— α-AgTlTe peritectic transformation (447 °C)
P_1 liq. + $<\beta$-AgTlTe$>$ $\leftrightarrows$ $<\alpha$-AgTlTe$>$
for compositions $<$ 50 mol% Ag_2Te

— 3-AgTlTe eutectoid transformation (400 °C)
E_2 $<\beta$-AgTlTe$>$ $\rightleftharpoons$ $<\alpha$-AgTlTe$>$ + $Ag_8Tl_2Te_5$
for compositions $>$ 50 mol% Ag_2Te

— two-phase region $<\alpha$-AgTlTe + β-AgTlTe$>$ between 447 and 400 °C

— β-AgTlTe congruent melting point (with a slight silver excess $Ag_{1.02}Tl_{0.98}T_2$, 483.5 °C)

III AgTlTe–Ag_2Te quasi-binary range 51–100 mol% Ag_2Te

— eutectic transformation for 68.5 mol% Ag_2Te (436 °C)
E_1 liq. $\leftrightarrows$ $<\beta$-AgTlTe$>$ + $Ag_8Tl_2Te_5$ (C)

— $Ag_8Tl_2Te_5$ (C) peritectoid transformation (440 °C)
P_2 Ag_3TlTe_2 + Ag_5TlTe_3 $\leftrightarrows$ $Ag_8Tl_2Te_5$

— Ag_5TlTe_3 (D) peritectoid transformation (446 °C)
P_3 Ag_3TlTe_2 + Ag_9TlTe_5 $\leftrightarrows$ Ag_5TlTe_3 (D)

— metastable Ag_3TlTe_2 (F) peritectic transformation (454 °C)
P_4 liq. + Ag_9TlTe_5 $\leftrightarrows$ Ag_3TlTe_2 (F)

— Ag_9TlTe_5 (E) peritectic transformation (504 °C)
P_5 liq. + $<\beta$-$Ag_2Te>$ $\leftrightarrows$ Ag_9TlTe_5 (E)

---

tion exists as a stable phase of the Ag_2Se–Tl_2Se system [17], the high-temperature unstable formation of Ag_3TlTe_2 (F) must be inferred. However, it has never been isolated at low temperatures nor has its formation been proved, except by the presence of an extra invariant. In that region, the overall heating effects correspond to the addition of stable and unstable equilibria (see Table 1).

Small deviations from the binary equilibria, probably due to tellurium vapour pressure under the samples inside the quartz tubes, give rise to extra heating effects assigned to the close ternary equilibria [3]. For example

near E_2, e_3 $$<\beta\text{-AgTlTe}> \underset{398\,^\circ\mathrm{C}}{\rightleftharpoons} <\alpha\text{-AgTlTe}> + Ag_8Tl_2Te_5 + Ag$$

near P_5, p_6 $$\text{liq.} + <\beta\text{-}Ag_2Te> \underset{502\,^\circ\mathrm{C}}{\rightleftharpoons} Ag_9TlTe_5 + Ag$$

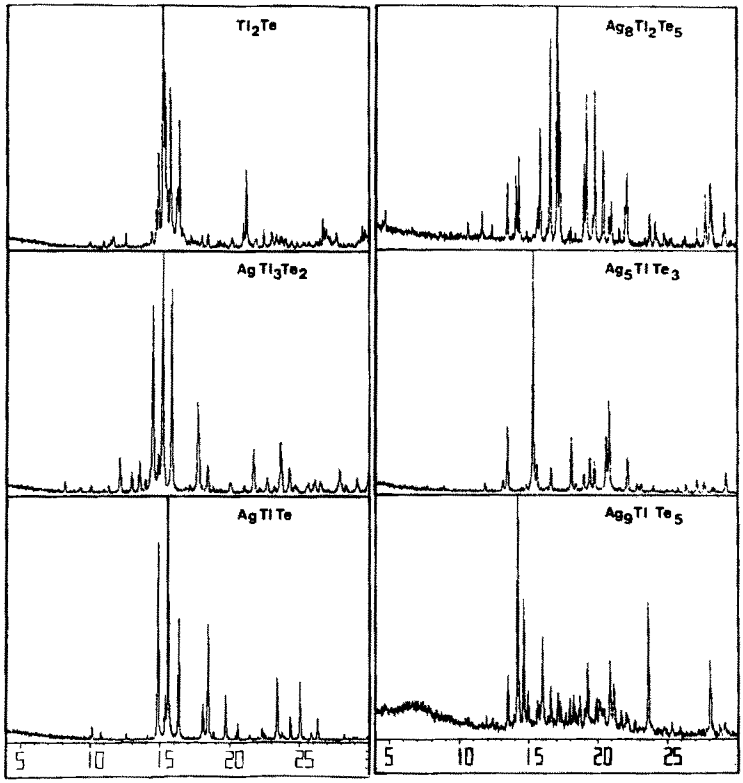

Fig. 4. X-ray diffraction patterns of the Tl_2Te–Ag_2Te system (θ) in Ag_9TlTe_5, three Si ($\theta = 14.23, 23.67, 28.09$) lines used as standard.

X-RAY DIFFRACTION (TABLE 2)

The structure of AgTlTe is well known. It has been described twice, first as stoichiometric AgTlTe [18] and later as having a silver lacunar composition [5]. Single crystals of the $AgTl_3Te_2$, $Ag_8Tl_2Te_5$ and Ag_9TlTe_5 compounds were isolated, the unit-cell parameters determined from Bragg, Weissenberg and precesion films, and refined by a least-squares program. The Ag_5TlTe_3 (D) compound was obtained as a single crystal grown by the Bridgmann technique from an ingot whose starting composition ($Ag_3Tl_{1.35}Te_3$) was outside the Ag_2Te–Tl_2Te system. The final composition of the crystal was determined by microprobe analysis with an accuracy of 2–3 wt%. The unit-cell parameters were determined and refined as for the other compositions. We have included the cell parameters of the compound $AgTlTe_2$, the only other phase of the Ag–Tl–Te ternary encountered in the AgTlTe–Te system. It is important to know the diffraction lines of that composition in order to determine if it is present in the melts solidified out of equilibria, as often happens when the annealing periods are too short.

TABLE 2

Structural data

Compound		Lattice parameters (pm)	Space group
AgTlTe	$Ag_{1+\epsilon}TlTe$	*a* 877.5(2) *b* 776.3(2) *c* 487.2(1)	Orth. *Pnam*
	$Ag_{0.92}TlTe$[5]	*a* 875.4(2) *b* 775.0(2) *c* 485.4(1)	
$AgTl_3Te_2$		*a* 988.0(5) *b* 1966.5(7) *c* 741.7(2)	Orth. *C*
Ag_5TlTe_3		*a* 1141.0(2) *c* 922.0(1)	Hex
$Ag_8Tl_2Te_9$		*a* 1869.9(2)	Cub. *F*
Ag_9TlTe_5		*a* 3052.0(2) *c* 1746.0(1)	Hex.
$AgTlTe_2$		*a* 993.0(1) *b* 8512.0(8) *c* 1702.09(2)	Orth. *C*
Ag_3TlTe_2[19]		*a* 460.0 *b* 476.0 *c* 1545.0	Orth. *Pnma*

One of the parameters (*b*) has a high value owing to a superstructure which increases it by a factor of ten. As a consequence, some characteristic X-ray diffraction lines are widened. Finally, the crystal structure of Ag_3TlTe_2 (F) was resolved by Avilov et al. [19] from a vapour-deposited, annealed sample.

Its existence is consequently uncertain, at least in the usual equilibria conditions.

THERMOELECTRIC POWER

These results (Fig. 3) can be considered as complementary, indicating the phases precisely, and with use as the basis for further physical measurements. An optimum value (either maximum or minimum) is roughly observed for every composition corresponding to a defined compound. Most of them are p-type conductors with a high absolute value of S (up to 780 $\mu V\ K^{-1}$ for AgTlTe). In a narrow range only, the composition $Ag_8Tl_2Te_5$ behaves as an n-type conductor. All the values are room temperature ones.

CONCLUSIONS

From a comparison of the data reported in refs. 3, 4 and 6 with those obtained in the present work (Fig. 2 and Table 1), our results confirm the general shape of the liquidus line and the existence of the 3 : 1, 1 : 1, 1 : 4 and 1 : 9 compounds suggested in refs. 3 and 4. However, we cannot confirm the formation of the 1 : 2 and 2 : 5 compounds suggested in ref. 6. The 1 : 5 compound (Ag_5TlTe_3, D) has never been obtained before, nor has the phase transformation of AgTlTe (B) been observed in relation with a narrow solid solution range, as seen here. Precise information concerning the Tl_2Te phase has explained the non-quasi-binary equilibrium of the 0–50% Ag_2Te area of the diagram.

REFERENCES

1 B. Pistoulet, D. Coquillat, J.C. Tedenac, G. Brun and M. Maurin, Phys, Status Solidi A, 77 (1983) 669.

2 R.M. Ayral-Marin, G. Brun, B. Liautard, J.C. Tedenac, D. Abdelhady, B. Pistoulet and M. Maurin, 1st. Europ. Conf. on Thermoelectrics, O.M. Rowe (Ed.), P. Peregrinus Ltd., U.K., 1988, p. 24.

3 M.B. Badanly and A.A. Kuliev, Rus. J. Inorg. Chem., 27(6) (1982) 867.

4 V.T. Abishov, M.B. Babanly and A.A. Kuliev, Russ. J. Inorg. Chem., 23(7) (1978) 1089.

5 R.M. Ayral-Marin, B. Liautard, M. Maurin, J.C. Tedenac and G. Brun, J. Phys. Chem. Solids, 49(8) (1988) 939.

6 W. Gawel, E. Zaleska and J. Terpilowski, J. Therm. Anal., 32 (1987) 227.

7 J.P. Bigot, Thesis, U.S.T.L., Montpellier, France, Oct. 1980.

8 V.P. Vasilev, A.V. Nikolskaya, Ya.J. Gerasimov and A.F. Kuznetsov, Izv. Akad. Nauk SSSR, Neorg. Mater., 4 (1968) 1040.

9 M.N. Abdulsalyamova and A. Abduraklimov, Dokl. Akad. Nauk Tadzh, SSR, 17 (1974) 42.

10 V.P. Vasilev, A.V. Nikolskaya and Ya.J. Gerasinov, in Thermodynamic Properties of Metal Alloys, Elm, Baku, 1974, p. 40 (in Russian).

11 V.P. Vasilev, author's abstract of candidate's dissertation, Moscow (1972).

12 M.M. Asadov, M.B. Babanly and A.A. Kuliev, Izv. Akad. Nauk SSSR, Neorg. Mater., 13(8) (1977) 1407.

13 A. Rabenau, A. Stegher and P. Eckerlin, Z. Metall., 51 (1960) 295.

14 M. Hansen, Consitution of Binary Alloys, McGraw Hill, New York, 1958.

15 R. Castanet, E. Bergman, M.L. Miche and H.V. Kehiain, Z. Metall., 68 (1977) 342; R. Castanet, E. Bergman and M. Gilbert, Z. Metall., 69(HS) (1978) 298, 1535.

16 A.S. Avilov, R.M. Imamov and Z.G. Pinsker, Sov. Phys. Cryst., 17(2) (1972) 237.

17 M.B. Babanly and A.A. Kuliev, Russ. J. Chem., 27(9) (1982) 1336.

18 J.C. Tedenac, B. Gardes, G. Brun, E. Philippot and M. Maurin, J. Solid State Chem., 33 (1980) 429.