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Thermodynamic and constitutional studies of the PbTe-GeTe system

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Some of the uncertainties concerning phase equilibria in the pseudo-binary system PbTe–GeTe have been clarified in this thermodynamic and constitutional investigation. The heats of fusion of PbTe, GeTe and $Pb_{0.2}Ge_{0.8}Te$ have been determined in a differential thermal analysis calorimeter. Based on these results and solution thermodynamics, the phase diagram of the system has been synthesized. Evidence for spinodal decomposition in this system has been presented for the first time with the aid of X-ray diffraction as well as transmission and scanning electron-microscopic data. The results are in confirmity with a pseudo-isomorphous system having a solid state miscibility gap.

1. Introduction

Several chalcogenide pseudo-binary systems have been investigated in recent years on account of their importance as electronic materials. Amongst these the system PbTe–GeTe has evoked considerable interest as well as some controversy with respect to phase equilibria. A knowledge of the exact phase relationships in this system is essential for the development of compound semiconductors with properties intermediate to and continuously varying between those of the individual components. The phase diagram of this system is, however, complicated by a minor difference in the crystal structures of the individual binary compounds at lower temperatures. PbTe has a cubic NaCl-type structure, but GeTe attains this structure only above about 400° C. Below this temperature GeTe crystallizes in a rhombohedral lattice, which represents a slight distortion of the high temperature cubic lattice.

Shelimova *et al.* [1] established the PbTe–GeTe phase diagram by thermal analysis and metallography. They reported it to be a eutectic-type phase diagram with the eutectic point at 20 mol % PbTe and 695° C. Mazelsky *et al.* [2] detected very limited mutual solubility between PbTe and GeTe up to 500° C on the basis of X-ray diffraction. These results are not consistent with those of Woolley and Nikolic [3], who reported the formation of a continuous series of solid solutions in samples quenched from 600° C. Recently, Hohnke et al. [4] have shown, on the basis of a re-interpretation of the results of Shelimova *et al.* [1], that the system is in fact pseudo-isomorphous with a congruently melting minimum around 20 mol % PbTe at 695° C (Fig. 1). They have also established a miscibility gap in the solid state by X-ray diffraction.

The present work was undertaken with a view to synthesizing the phase diagram of this system on the basis of heats of fusion and solution thermodynamics. Towards this end it was proposed to determine the heats of fusion of PbTe, GeTe and $Pb_{0.2}Ge_{0.8}Te$ in a differential thermal analysis calorimeter.

At the beginning of this study it was noted with interest that Darrow *et al.* [5] had detected spinodal decomposition in the ionic alloys of the system PbS–PbTe. This was perhaps the first instance where evidence for the modulated structure was obtained from amongst the many known chalcongenide quasi-binary systems. In view of the existence of a miscibility gap in the PbTe–GeTe system, it was considered worthwhile to study the

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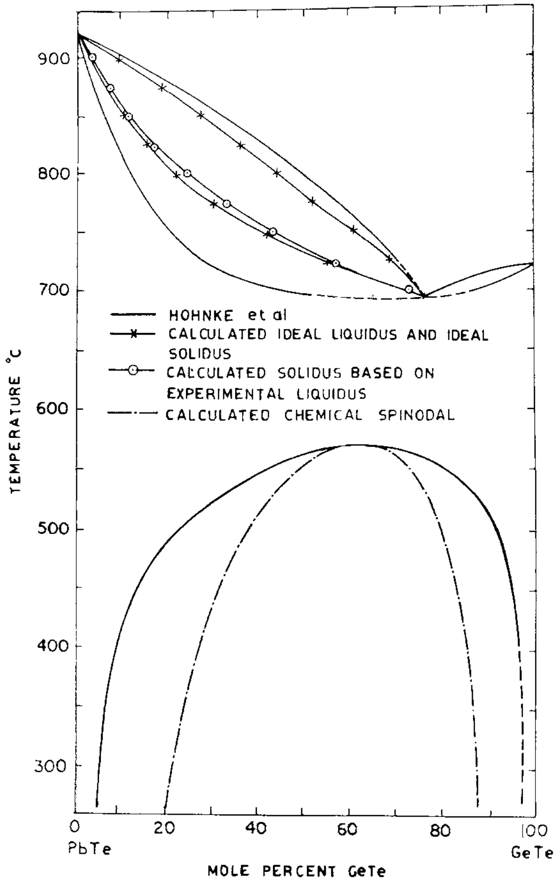


Figure 1 Phase diagram of quasi-binary PbTe–GeTe system.

decomposition behaviour of alloys quenched from the single-phase solid-state region as well as the melt and to look for any possible occurrence of spinodal decomposition in this system with the aid of X-ray and electron-microscopic techniques.

2. Experimental

2.1. Materials

High-purity lead and tellurium, each 99.99% pure (obtained from the Bhabha Atomic Research Centre, Bombay), and specpure germanium (supplied by Johnson Matthey, England) were used in this investigation.

2.2. Preparation of alloys

A series of ternary alloys containing 30, 40, 50, 60, 65, 70 and 80 mol% GeTe were used in the present study. The alloys were prepared from the constituent elements in evacuated and sealed silica capsules. The capsules were heated at a rate of 200° C h^{-1} held for 1 h at 960° C, thoroughly shaken and then quenched into water at room temperature. Each alloy was chemically analysed for actual composition.

2.3. Calorimetric measurements

The heats of fusion of PbTe, GeTe and $Pb_{0.2}Ge_{0.8}Te$ were determined in a locally fabricated Differential Thermal Analysis Calorimeter, details of which have been published elsewhere [6]. Each time 1.5 cm^3 of a thorough mixture of fresh powders (– 150 mesh) of lead and tellurium, germanium and tellurium or lead, germanium and tellurium corresponding to the stoichiometric composition of PbTe, GeTe or $Pb_{0.2}Ge_{0.8}Te$, respectively, was taken in a graphite sample container. A chromel–alumel thermocouple was embedded in it, but was protected from the attack of the melt by a silica tube. After inserting the container, the silica well was evacuated and purged three times with purified argon.

The furnace block of stainless steel was heated from room temperature to beyond the melting point of the compound at the rate of 3° C min^{-1} by controlling the input voltage through a voltage stabilizer and a dimmerstat. The temperature of the block (T) and the differential temperature between the sample and the reference block (ΔT) were noted at intervals of 30 sec. In each case, at the initial stage of the run there was an exothermic peak due to the formation of the compound from its component elements. After the reaction resulting in compound formation was complete, the product was heated beyond the melting point. During the fusion of PbTe, GeTe and $Pb_{0.2}Ge_{0.8}Te$ a sharp endothermic peak was observed, from the area of which the heat of fusion could be calculated. The calorimeter was calibrated by studying the fusion of pure germanium, potassium bromide and germanium telluride.

2.4. Solid state decomposition

The as-cast lumps were ground to fine powder and then resealed in 3 mm diameter silica capsules. A number of these capsules were held at 660° C for 1 week and subsequently quenched in water. The resulting samples were aged in preliminary experiments in the range of 100 to 350° C at temperature intervals of 50° C for different lengths of time varying from a few minutes to several hours, and then quenched. These studies indicated that the high temperature single phase could be retained by quenching from 660° C in all PbTe–GeTe alloys except in that containing 60 mol % GeTe. Ageing of the single phase alloys for a few minutes at the high temperatures resulted in the appearance of side bands. Continued ageing led to phase separation and decomposition into PbTe and GeTe. To give some idea of the kinetics of decomposition, the PbTe–65 mol % GeTe alloy decomposed completely in 2 min at 350° C, $\frac{1}{2}$ h at 300° C, 4 h at 250° C and 24 h at 200° C, whereas a temperature of 100° C was insufficient for complete decomposition even in 10 days.

In the light of above preliminary investigations the ageing temperature of 200° C was chosen and is considered to represent an optimum temperature where the kinetics of the decomposition process was sufficiently slow to permit the observation of the decomposition step by step, but fast enough to achieve complete decomposition within the reasonable period of 24 h. Hence for the kinetic studies on two alloys containing 65 and 30 mol % GeTe, the samples homogenized at 660° C were directly quenched into a salt bath (ICI, Crescent TS-150) at 200° C and aged for different lengths of time ranging from 2 min to 24 h. They were finally quenched in water at room temperature.

2.5. Quenching from the melt

As summarized in a number of recent reviews [7–10], quenching alloys from the liquid state can lead to one or more of the following important effects:

(a) shift of solid solubility limit to higher solute concentrations;

(b) retention of high-temperature phases at room temperature;

(c) formation of new intermediate phases;

(d) production of amorphous alloys.

These effects arise as a result of the spectacularly high cooling rates of 10^6 to 10^8 ° C sec^{-1} attained in these experiments.

The aim of using this technique in the present investigation was manifold. Firstly, the ability of the technique to retain high-temperature phases could be exploited. Secondly, this technique could prove quite useful in studying the early stages of spinodal decomposition, if any, as amply demonstrated by Agarwal and Herman [11]. Lastly, this technique is time-saving unlike the prequenching solid-state homogenizing of alloys at elevated temperatures, which requires a very long time. It is relevant to recall here that Hohnke *et al.* [4] could not produce a single phase in 60 mol % GeTe alloy by traditional quenching.

Alloy samples of about 500 mg were quenched from the liquid state in the present work using the "gun" technique. The experiment consisted of melting the alloy in a graphite crucible with a narrow orifice at the bottom and ejecting it through this opening by means of a shock wave generated by the rupture of a "mylar" diaphragm under the influence of high pressure gas. The ejected alloy is highly atomized and impinges on a ski-slope copper substrate and cools rapidly. The details of the experimental apparatus have been described elsewhere [12]. The resulting foil or powder was aged in oil bath (HHV, Rotary pump oil) at 100° C from 10 minutes to one week.

2.6. X-ray analysis

The samples quenched from the melt and the solid state were analysed by X-ray diffraction using a 11.46 cm diameter Debye–Scherrer camera and filtered CuKα radiation from a Phillips X-ray Generator. The diffraction patterns were analysed for intensity variations using a microdensitometer (Model XM 102, National Spectrographic Laboratories, Cleveland, Ohio).

2.7. Electron microscopy

Electron-metallographic examination of the samples was carried out using both scanning and transmission techniques. In view of the brittle nature of the sample it was extremely difficult to produce thin foils by the customary techniques. Instead, the alloy was ground to – 200 mesh and a small quantity of it was suspended in distilled water at room temperature for 24 h. A portion of the thin film floating on the surface of the water was carefully collected on a grid having a thin film of collodion or formvar on it. Transmission studies were carried out at 40 kV using a Philips EM 200 microscope. Freshly fractured surfaces of suitably heat-treated bulk samples were examined at 20 kV in a Siemens Autoscan scanning electron microscope.

3. Results and discussion

3.1. Heat of fusion and phase diagram

The heat of fusion, ΔH^{f} of PbTe and GeTe obtained in this investigation are 9.9 ± 0.3 and 15.0 ± 0.5 kcal mol^{-1}, respectively, which are in reasonable agreement with the values of 9.4 and 14.8 kcal mol^{-1} respectively, reported by Steininger

[13]. The heat of fusion of $Pb_{0.2}Ge_{0.8}Te$ is 13.4 ± 0.5 kcal mol^{-1}, which compares well with the value of 14.0 kcal mol^{-1}, obtained by the *pro rata* addition of the heats of fusion of PbTe and GeTe. The heat of fusion of this congruently melting composition may be calculated by an analysis due to Wagner [14] involving a consideration of the excess free energy difference between the solid and liquid phases. This analysis is valid when both the liquid and solid phases are regular solutions. The heat of fusion of $Pb_{0.2}Ge_{0.8}Te$ estimated by such an analysis is 13.2 kcal mol^{-1}. The good agreement with our experimental value indicates that in the system PbTe–GeTe both the solid and liquid phases may conform to the regular solution model.

It has already been pointed out that Hohnke *et al.* [4] established the existence of a miscibility gap in the solid state and replotted the data of Shelimova *et al.* [1] as a pseudo-isomorphous system with a congruently melting minimum at $Pb_{0.2}Ge_{0.8}Te$ and 695° C. The solidus plotted by the latter investigators is not consistent with thermodynamics since there is a long horizontal line near the congruently melting composition, which apparently violates the phase rule.

In order to determine the correct profile of the phase diagram, the solidus and the liquidus were synthesized by using the following relationships, valid for ideal solutions, for both the solid and liquid phases [15]:

$$\ln \frac{X_B^s}{X_B^l} = \frac{\Delta H_B^f}{R}\left[\frac{1}{T} - \frac{1}{T_{mB}}\right] \qquad (1)$$

and

$$\ln \frac{X_A^s}{X_A^l} = \frac{\Delta H_A^f}{R}\left[\frac{1}{T} - \frac{1}{T_{mA}}\right] \qquad (2)$$

where subscripts A and B denote the components and T_m is the melting point, X^s and X^l are compositions (mol fractions of solute) of solid and liquid, respectively, which are in equilibrium at a temperature T.

The phase diagram was split into two isomorphous segments, namely $PbTe$–$Pb_{0.2}Ge_{0.8}Te$ and $Pb_{0.2}Ge_{0.8}Te$–$GeTe$, and each synthesized independently using Equations 1 and 2. Our experimental values of the heats of fusion were used in above calculations. The ideal liquidus, the ideal solidus and the solidus based on the experimental liquidus of Shelimova *et al.* [1] have been synthesized and shown in Fig. 1. The experimental liquidus shows a slight positive deviation from ideality. The experimental solidus, however, shows a pronounced positive deviation which is obviously due mainly to errors introduced by supercooling of the melt and coring effects associated with thermo-analytical techniques of establishing solidus through cooling cycles. Part of the discrepancy may also be due to the instability of the solid phase relative to the ideal solution conditions. This instability may also be inferred from the solid state decomposition of the alloys at low temperatures indicated by the miscibility gap.

3.2. Constitution in the solid state

Fig. 1 also shows the experimentally determined solvus, and the chemical spinodal calculated from it by the method of Cook and Hilliard [16]. The coherent spinodal could not be estimated due to the non-availability of the values of elastic constants of GeTe and the lack of any knowledge regarding their dependence on the concentration of PbTe in the alloys. The studies of Darrow *et al.* [5] on the system PbS–PbTe have shown clearly that such data as well as the temperature dependence of elastic constants can play a very significant role in the estimation of the correct coherent spinodal in chalcogenide systems.

3.2.1. Decomposition of solid state-quenched alloys

X-ray analysis of samples quenched from 660° C into water at room temperature showed the presence of only the high temperature phase. Annealing the sample at 200° C resulted in the appearance of side bands in the X-ray diffraction patterns. Since such an effect could be caused by the progress of a spinodal decomposition, the development of the satellites was followed carefully. The intensity of the satellite reflections increases as a function of ageing time, attaining a peak value after approximately 8 h in case of the alloy containing 65 mol % Ge Te. Further ageing at this temperature leads to a phase separation. Fig. 2 shows the variation of diffraction intensity of the (2 0 0) reflection as a function of the diffraction angle for different annealing times in case of the 65 mol % Ge Te alloy.

The behaviour of the alloy with 30 mol % GeTe was identical to that of the 65 mol % GeTe alloy, but for the difference in the location of the satellite reflections. While the reflections were nearly symmetrically situated with reference to

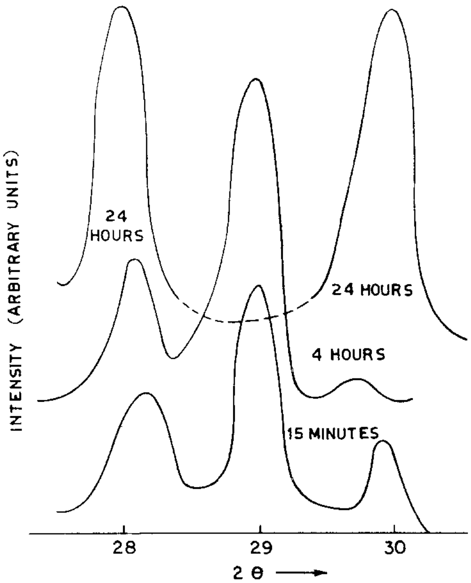


Figure 2 Microdensitometer plots of (2 0 0) reflections from PbTe–65 mol% GeTe alloy (solid state quenching).

the main reflections in the latter, there was a pronounced asymmetry in the former.

The values of wavelength for the composition fluctuation (λ) were calculated using the Daniel–Lipson relation [17]:

$$\lambda = \frac{a.h.\ \tan\theta}{(h^2 + k^2 + l^2)\cdot\delta\theta} \tag{3}$$

where a is the lattice constant $(h\,k\,l)$ are the Miller indices of the reflections used and θ is the corresponding Bragg angle and $\delta\theta$ is a measure of the separation of the satellites. The first resolvable satellite obtained in the 65 mol % GeTe alloy gave wavelength values of about 1000 Å, while at the maximum separation a value of about 100 Å was obtained. The magnitudes of these values correspond well with those reported in literature [5].

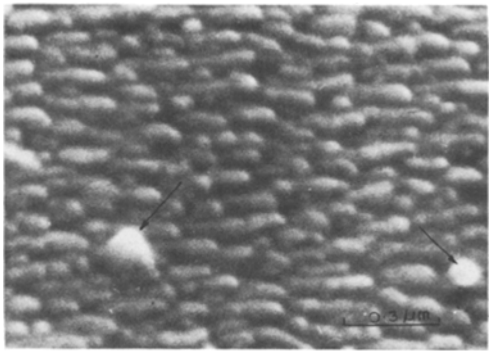
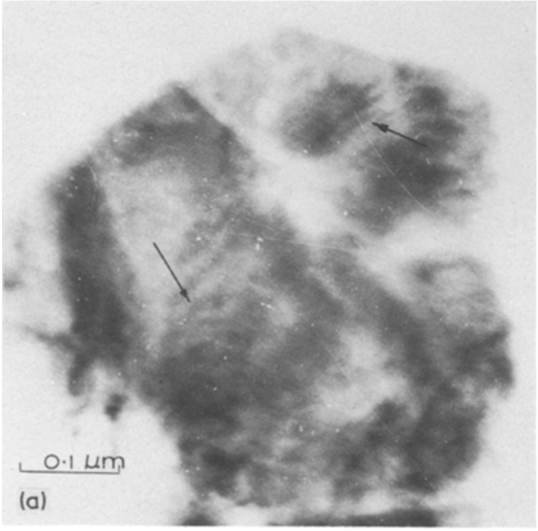


Figure 4 Scanning electron micrograph of PbTe–65 mol % GeTe alloy. Treatment as for sample of Fig. 3.

Both scanning and transmission electron micrographs reveal the presence of a modulated structure in the alloy containing 65 mol % GeTe, aged for 8 h at 200° C (Fig. 3). The periodicity of the modulated structure was found to be about 850 ± 150 Å. These values are in the range 400 to 1000 Å reported by Darrow *et al.* [5] for PbS–PbTe alloys. They also agree with the X-ray results. Another noteworthy feature is the difference in orientation of the rods in different grains as clearly brought out in Fig. 3. The orien-



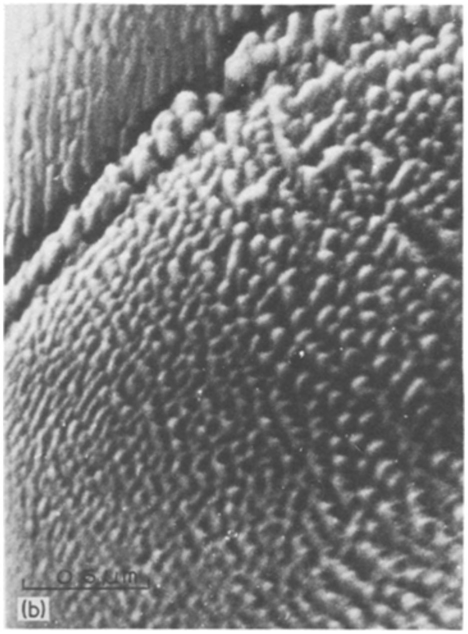


Figure 3 Microstructure of PbTe–65 mol % GeTe alloy, homogenized at 660° C for 1 week and aged for 8 h at 200° C. (a) Transmission electron micrograph, (b) scanning electron micrograph.

tation relationships could not, however, be satisfactorily established owing to the difficulty in obtaining clear transmission electron micrographs, partly because of heavy absorption by PbTe and partly due to the very limited regions capable of transmission. In certain areas of the fractured surface there was evidence for the existence of isolated precipitate particles (Fig. 4).

3.2.2. Decomposition of liquisol-quenched alloys

The results obtained justified the use of liquisol quenching. It was possible to retain a single phase in the entire composition range. No difficulties similar to those reported by Hohnke *et al.* [4] were encountered even in the alloy containing 60 mol % GeTe. X-ray studies were carried out on the as-quenched sample and on samples transformed at 100° C. While it would have been ideal to study the decomposition behaviour at 200° C for the sake of comparison with the results obtained on the solid-state quenched samples, it was found that complete decomposition of a PbTe–65 mol % GeTe alloy results in just 10 min at 200° C. A temperature of 100° C, though too low to lead to complete decomposition even after one week, was ideally suited for studying the onset and movement of side bands. The reason for the increased rate of decomposition of the liquisol quenched foils probably lies in the enhancement of diffusion as a result of super saturation of vacancies obtained by liquisol quenching. It was noted that the side bands first appeared after annealing for 10 min and moved to the greatest separation in 2θ of 1.00° and 1.05° towards low-angle and high-angle sides respectively in 20 min. Microdensitometer traces of the (2 0 0) reflections of the cubic phase are shown in Fig. 5 at various stages of the decomposition process. The values of the wavelength calculated using Equation 3 are once again in the range 100 to 1000 Å, the actual value depending on the ageing time at the chosen temperature.

Even though it would have been helpful to corroborate the above conclusions with transmission electron microscopy, the splats were unfortunately not thin enough to permit transmission work owing to the high absorption factor of lead. Attempts are being made to develop a suitable thinning procedure for examination of the liquisol-quenched foils.

While the present results support the possible existence of a spinodal mode of decomposition in alloys of this system, it may be worthwhile to follow the kinetics and nature of decomposition of the alloys outside the calculated spinodal for confirmatory evidence.

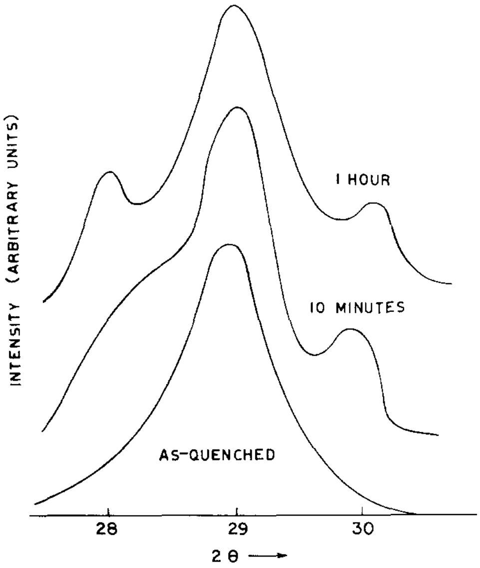


Figure 5 Microdensitometer plots of (2 0 0) reflections from PbTe–65 mol % GeTe alloys (quenched from the melt).

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