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# Determination of the liquidus-solidus curves for the system PbTe–GeTe

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The liquidus and solidus curves for the PbTe–GeTe system were determined by DTA over the entire compositional range. The samples were annealed for one month at 600°C and rapidly quenched. X-ray data for the annealed-quenched samples indicated that solid solution exists across the entire compositional range. Unannealed samples indicated the presence of different phases.

## 1. Introduction

Both detectors and lasers [1-4] have recently been made using $Pb_{1-x}Ge_xTe$ single crystals for values of $x$ ranging from 0.015 to 0.10. In addition $Pb_{1-x}Ge_xTe$ material for values of $x$ ranging from 0.30 to 0.60 have been considered by us for possible use as PTC material based on dielectric anomalies at the ferroelectric Curie temperature [5]. The growth of these crystals required a thorough understanding of phase relationships for the PbTe–GeTe system. Although several studies of this system are reported in the literature [6-9] only that of Shelimova *et al.* [6] examined the liquidus and solidus curves. Shelimova *et al.* interpreted their data as implying eutectic formation with limited solid solubility everywhere below the 700°C eutectic temperature. Mazelsky *et al.* [7] confirmed limited solubility of GeTe in PbTe at temperatures up to 500°C, while Woolley and Nikolic [8] showed complete solubility between PbTe and GeTe in samples quenched from 600°C. Recently, Hohnke *et al.* [9] have presented data suggesting that the limited solubility zone extends only up to 570°C with ex-solution occurring in the solid state over a wide compositional range.

Selection of the most appropriate technique for homogeneous crystal growth required accurate knowledge of the liquidus and solidus compositions at different temperatures. Efforts to grow homogeneous, single crystals based on the data of Shelimova *et al.* were unsuccessful [10]. Hence, we have re-examined the liquidus and solidus portion of the phase diagram using samples annealed at 600°C and rapidly quenched.

## 2. Experimental

The various $Pb_{1-x}Ge_xTe$ samples were prepared by weighing the desired amounts of 99.9999% pure Pb, Ge and Te (further zone refined by us) into 8 mm i.d. tubes to give 10 g charges. The tubes were sealed under a vacuum of $10^{-6}$ Torr, heated to 1000°C in a rocking furnace, maintained at this temperature for 2 h, then oil quenched. The quenched samples were then ground to $< 75$ μm powders and small portions were sealed at $10^{-6}$ Torr in 4 mm i.d. quartz tubes. These samples were then annealed at 600°C for 1 month and water quenched. Electron microprobe analysis of as-compounded material and the annealed-quenched material showed the composition to be identical within the accuracy of the determination. Portions of each sample were taken for DTA and X-ray specimens. Samples of the as-compounded ingots and 680°C annealed powders were also studied in some instances.

The differential thermal analyser was a DuPont Model 900 with Pt–(13% Rh–Pt) thermocouples. DTA samples weighing ~ 50 mg were sealed in quartz tubes at $10^{-6}$ Torr. The reference material was high purity $Al_2O_3$ calcined at 1800°C. Programmed heating rates of 5°C $min^{-1}$ and cooling rates of 3°C $min^{-1}$ were used. DTA traces were recorded for each sample for 2 to 3 heating-cooling cycles and separate repeat runs were made for each composition. The temperature of the first deviation from the baseline on the initial heating cycle was taken as the solidus temperature. Likewise, the temperature of the first deviation from the baseline during cool-down was accepted as the liquidus temperature. The DTA values were found to be reproducible within ± 5°C.

Standard X-ray diffraction or Debye-Scherrer powder patterns were made on samples ground to 100 μm or less. Cu*Kα* radiation was used and exposure times of up to 8 h were utilized.

## 3. Results and discussion

The liquidus and solidus curves for the PbTe–GeTe system as determined by us and by Shelimova *et al.* [6] are shown in Fig. 1, along with the miscibility gap data reported by Hohnke *et al.* [8]. Both our observed data and phase diagram classification differ from those of Shelimova *et al.* It should be pointed out that the solidus-liquidus curves shown by Hohnke *et al.* were not determined by them but was a modification of Shelimova's data to explain the complete solid solubility over the entire composition. While the differences might seem minor, the differences particularly in the solidus temperatures greatly influenced our ability to grow crystals by a vapour transport method [10]. For example we were able to grow crystals for various concentrations of GeTe from 0.04 to 0.10 mole fraction at temperatures which would have been impossible had the data of Shelimova *et al.* been accurate because the system would have been in a region containing both liquid and solid. Our minimum in the solidus temperature of about 681°C was also slightly lower than their reported eutectic temperature of 700°C. Also, more samples of different compositions were made by us so the curves were better defined. These differences between our data and those of Shelimova *et al.* are probably caused by the differences in the thermal history of the samples because they did not anneal most of their samples and those samples which were annealed were probably not quenched rapidly enough [9]. The discovery by Hohnke *et al.* that ex-solution in the solid state occurs over a wide compositional

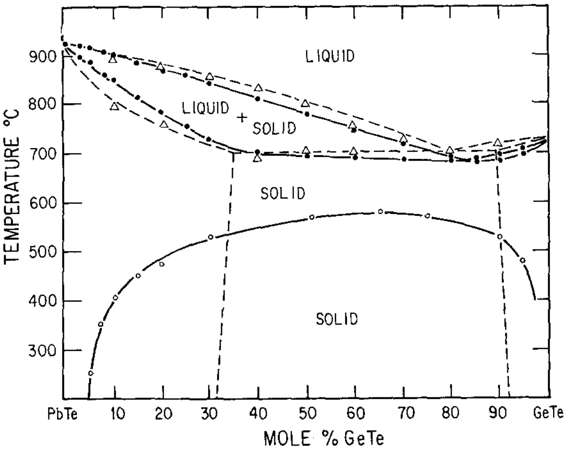

*Figure 1* Phase diagram for the PbTe–GeTe system. ●, our data; ○, Hohnke *et al.* [9]; △ Shelimova *et al.* [6].

TABLE I Thermal deviations from base line of DTA for the PbTe–GeTe system

| Composition | Temperature (°C) | | | | |
|---|---|---|---|---|---|
| | Liquidus | Solidus | Other transitions | | |
| GeTe | 724 | (724) | | | |
| 95% GeTe | 707 | 698 | 565$^{c}$ | 370$^{c}$ | 270$^{h}$ |
| 90% GeTe | 695 | 685 | 580$^{c}$ | 340$^{c}$ | 296$^{c}$ |
| 85% GeTe | 690 | 683 | 570$^{c}$ | | 296$^{h,c}$ |
| 80% GeTe | 693 | 681 | 580$^{c}$ | 320$^{c}$ | 296$^{c}$ |
| 70% GeTe | 720 | 685 | 590$^{c}$ | | 296$^{c}$ |
| 60% GeTe | 740 | 690 | 594$^{c}$ | | 296$^{c}$ |
| 50% GeTe | 780 | 695 | | | |
| 40% GeTe | 810 | 700 | 695 | | |
| 30% GeTe | 842 | 730 | 695 | | |
| 25% GeTe | 858 | 754 | 695 | | |
| 20% GeTe | 872 | 785 | 695 | | |
| 15% GeTe | 886 | 815 | 695 | | |
| 10% GeTe | 902 | 850 | 695 | | |
| 8% GeTe | 909 | 860 | | | |
| 5% GeTe | 915 | 885 | | | |
| 3% GeTe | 918 | 895 | | | |
| PbTe | 924 | 924 | | | |

$^{c}$Transitions observed during cool-down.
$^{h}$Transitions observed during heat-up.

range at temperatures below 570°C would explain how one could indeed find two phases or crystal structures in a system which was cooled slowly. Table I gives the thermal deviations from the base line during DTA determinations for numerous PbTe–GeTe compositions.

The X-ray diffraction data on the annealed-quenched samples showed the presence of solid solution over the entire compositional range in agreement with others [8, 9]. Fig. 2 illustrates how the lattice constant varied as a function of composition. The data of Hohnke *et al.* [9] and Wolley *et al.* [8] are also shown in Fig. 2. Our data agree more closely with those of the former. The differences in the lattice constants among the various workers were probably caused by differences in the annealing and quenching conditions. Table II lists the lattice parameter data with estimated standard deviations in parentheses. The changes in rhombohedral or interaxial angle with composition are also shown in Fig. 2 with the data listed in Table II. Differences between interaxial angle values and those of Hohnke *et al.* are probably caused by differences in the thermal history of the samples.

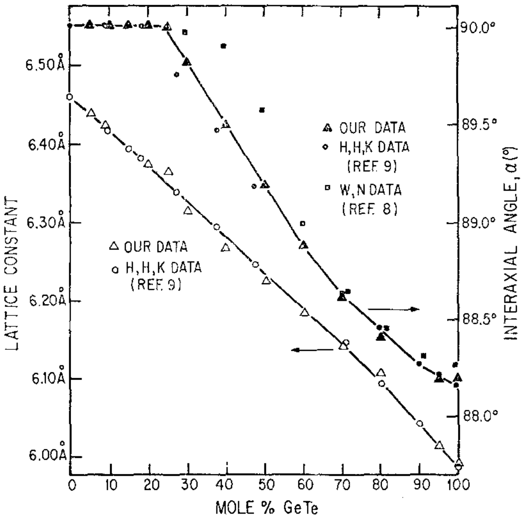

*Figure 2* Lattice constant and interaxial angle as a function of the mol % GeTe present.

TABLE II Lattice parameters of $Pb_{1-x}Ge_xTe$ for various values of $x$

| Values of $x$, (mole fraction GeTe) | Lattice constant, $a$ (Å) | Interaxial angle, α (degs.) |
|---|---|---|
| 1.00 | *5.987 (0.006)† | 88.19 (0.05)† |
| 0.95 | *6.012 (0.006) | 88.20 (0.04) |
| 0.80 | *6.103 (0.008) | 88.41 (0.04) |
| 0.70 | *6.142 (0.007) | 88.62 (0.05) |
| 0.60 | *6.183 (0.008) | 88.88 (0.05) |
| 0.50 | *6.225 (0.008) | 89.19 (0.06) |
| 0.40 | *6.265 (0.008) | 89.50 (0.07) |
| 0.30 | *6.315 (0.008) | 89.82 (0.06) |
| 0.25 | 6.361 (0.007) | 90.0 |
| 0.20 | 6.374 (0.006) | 90.0 |
| 0.15 | 6.395 (0.004) | 90.0 |
| 0.10 | 6.414 (0.005) | 90.0 |
| 0.05 | 6.438 (0.005) | 90.0 |

*Rhombohedral structure.
†Standard deviations given in parentheses.

Differential thermal analysis (DTA) of many samples as compounded, which were not annealed and quenched, gave data which indicated an eutectic temperature at 690 to 700°C during both heat-up and cool-down; yet annealed samples of the same compositions gave no evidence of an eutectic during the heat-up cycle. However, even annealed samples containing 15 mol % or more of GeTe gave indications of an eutectic during the cool-down of a DTA run. Repeat DTA runs on the same sample gave indications of an eutectic both upon heating and cooling. If relatively rapid and non-equilibrium cooling from the melt occurred during either compounding or DTA runs, the final temperature of solidification could be much lower than it would be for equilibrium conditions [11]. The solid phase from a non-equilibrium system would not be homogeneous because of the slow diffusion rate of the two components in the mixture. This could explain the presence of a material melting at about 700°C for samples cooled under non-equilibrium conditions. Samples annealed at 680°C then rapidly quenched gave DTA traces which were almost identical to those obtained on samples which were annealed at 600°C.

Table I gives the thermal changes for various compositions as indicated by DTA measurements. The liquidus and solidus temperature points were readily identified but other specific phase changes could not be determined with certainty. As mentioned previously, there was a change which occurred at 690 to 700°C on cool-down which was thought to be related to the non-equilibrium kinetics of the system. X-ray diffraction data on those samples from DTA experiments which showed thermal changes at 690 to 700°C also showed that two crystal structures, cubic and rhombohedral, were present. X-ray diffraction studies on annealed-quenched samples before the DTA runs showed the presence of only one phase or crystal structure. An examination of the phase diagram in Fig. 1 and the data in Table II can explain the presence of two structures. Ex-solution in the solid phase could lead to two phases or structures as the samples were cooled. Also, if non-equilibrium solidification occurred then some of the material which freezes out may be of such a composition that it has a different structure from other parts of the solid phase.

Compositions containing 60 to 95 mol % GeTe showed transformations during the cool-down of DTA at 565 to 595°C which might be the temperatures at which ex-solution occurred as suggested by Hohnke *et al.* The fact that these temperatures are somewhat greater than those of Hohnke *et al.* was probably caused by differences in quenching rates. X-ray diffraction on these samples after the DTA runs indeed showed the presence of both cubic and rhombohedral phases which would support the ex-solution theory.

Some thermal changes were also observed at 320 to 370°C on samples containing 60 to 95% Ge. These changes may be due to transformations in crystal structures. It has been reported that GeTe transforms from a cubic to rhombohedral structure at 365°C [12] although no data have been reported for concentrations greater than 0.2 mole fraction GeTe. Extrapolated data [9] on transition temperatures as a function of composition indicate that thermal deviations observed by us at 320 to 365°C may be caused by phase transformations from cubic to rhombohedral structures. Because the transition temperatures for a given composition would change with the annealing treatment [12], one might expect our DTA cooled samples to give erratic transition temperatures as was observed.

The thermal changes at 296°C are not explainable in terms of any known behaviour of the PbTe–GeTe system. However, X-ray diffraction on a few samples from DTA experiments indicated that two rhombohedral structures were sometimes present. It is possible that these changes which occur at 296°C are caused by transformations between the two rhombohedral phases. Certainly, more data are needed to identify the exact cause of the thermal deviations in the DTA curves for those deviations other than those of the solidus and liquidus.

## 4. Conclusions

The liquidus and solidus curves for the PbTe–GeTe system were determined by DTA over the entire compositional range. The samples were annealed for one month at 600°C and rapidly quenched in water. These curves are quite different from those reported previously in that the earlier data indicated limited miscibility and the formation of an eutectic on samples which were not annealed and rapidly quenched. X-ray diffraction data for the annealed-quenched samples indicated that solid solution exists over the entire compositional range in agreement with the results of others. Thermal deviations from the base line during DTA runs occurred for other than the solidus and liquidus points. Most of these deviations can be explained by non-equilibrium conditions during cool-down, by ex-solution in the solid state and by possible crystal structure transitions. This work points out the dangers involved in using non-equilibrium methods as DTA for determining phase diagrams. Reliable data can be obtained if the samples are well equilibrated before use.

## References

1. G. A. ANTCLIFFE, S. G. PARKER and R. T. BATE, *Appl. Phys. Letters* **21** (1972) 505.
2. J. S. WROBEL, G. A. ANTCLIFFE and R. T. BATE, Conference on Physics of Semimetals and Narrow Band Semiconductors, Philadelphia, 1971, to be published in *J. Non Metals.* **1** (1973) 217.
3. G. A. ANTCLIFFE, R. T. BATE, S. G. PARKER and J. S. WROBEL, Electrochemical Society, Houston, Texas, Abst. No. 205, (1971) p. 521.
4. I. MELNGAILIS and T. C. HARMAN, *Lincoln Lab., Solid State Res.* **1** (1972) 7.
5. B. M. KULWICKI and A. J. PURDES, *Ferroelectrics* **1** (1970) 253.
6. L. E. SHELIMOVA, N. KH. ABRIKOSOV and V. I. BESSONOV, *Izv. Akad. Nauk. SSR, Metal. i. Gornae Delo* **1** (1964) 180.
7. R. MAZELSKY, M. S. LUBELL and W. E. KRAMER, *J. Chem. Phys.* **37** (1962) 45.
8. J. C. WOOLLEY and P. NIKOLIC, *J. Electrochem. Soc.* **112** (1965) 82 and **112** (1965) 906.
9. D. H. HOHNKE, H. HOLLOWAY and S. KAISER, *J. Phys. Chem. Solids* **33** (1972) 2053.
10. S. G. PARKER, J. E. PINNELL and R. E. JOHNSON, *J. Electronic Mats.* **3** (4) in press.
11. F. H. GETMAN and F. DANIELS, "Outlines of Physical Chemistry", (John Wiley, New York, 1946) p. 330.
12. L. E. SHELIMOVA, N. KH. ABRIKOSOV and V. V. ZHDANOVA, *Russ. J. Inorg. Chem.* **10** (1965) 650.

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