Journal of Optoelectronics and Advanced Materials Vol. 7, No. 4, August 2005, p. 1977 - 1981

PARTIAL PAIR CORRELATION FUNCTIONS OF AMORPHOUS AND LIQUID $Ge_{15}Te_{85}$

I. Kaban, P. Jóvári[a], W. Hoyer[*]

Chemnitz University of Technology, Institute of Physics, D-09107 Chemnitz, Germany
[a]Research Institute for Solid State Physics and Optics, Konkoly-Thege u. 29-33, H 1121 Budapest, Hungary

X-ray and neutron diffraction study of amorphous and liquid $Ge_{15}Te_{85}$ alloys has been carried out. The experimental data have been simulated with the reverse Monte-Carlo technique and the partial pair correlation functions were derived. Analysis of the experimental and modelled results showed that there exist similarities between the amorphous and low-temperature liquid structure. The temperature induced structural transformations in liquid $Ge_{15}Te_{85}$ are connected with the changes in $g_{TeTe}(r)$ and $g_{GeTe}(r)$ and they are more pronounced close to the melting point.

(Received July 4, 2005; accepted July 21, 2005)

Keywords: Liquid and amorphous $Ge_{15}Te_{85}$, Structure factors, Pair correlation functions

1. Introduction

Liquid $Ge_{15}Te_{85}$ eutectic alloy exhibits peculiar temperature dependence of the physical properties. For example, the electrical resistivity for the liquid $Ge_{15}Te_{85}$ decreases by nearly two orders of magnitude within ~100 °C above the eutectic temperature ($T_{eut.} \approx 375$ °C) [1, 2]. The temperature dependence of the dynamic viscosity of liquid $Ge_{15}Te_{85}$ alloy shows positive deviations from the Arrhenius plot below ~525 °C [3]. The specific heat, isothermal compressibility and thermal expansion determined as functions of temperature showed extrema at ~100 °C above the eutectic temperature [4]. The anomalous behaviour of the physical properties of molten $Ge_{15}Te_{85}$ has been explained by existence of some structural units and by the structural changes occurring with variation of the temperature (e.g. [1-7]). But there is not a unique point of view on this problem so far.

Amorphous chalcogenides based on Ge and Te (Ge-Sb-Te, Ge-As-Te etc.) are of a high industrial interests due to such physical phenomena as electric switching [8] and optical phase change recording [9]. For understanding of the multicomponent systems knowledge of binary Ge-Te alloys is required. However, in spite of a number of research works carried out so far (e.g. [10-14]) the atomic structure of amorphous $Ge_{15}Te_{85}$ is still not completely known.

In the present work we perform the experimental investigations of liquid and amorphous $Ge_{15}Te_{85}$ with X-ray and neutron diffraction and model atomic structure with the help of reverse Monte Carlo simulation technique [15].

2. Experimental

Ge and Te pieces of high purity (99.999 %) were used for preparation of $Ge_{15}Te_{85}$ samples by melting at 800 °C in evacuated and sealed quartz ampoules. The amorphous $Ge_{15}Te_{85}$ alloy was obtained by the melt spinning technique.

Neutron diffraction experiments were carried out with the liquid and amorphous materials diffractometer SLAD at NFL, Studsvik [16]. The samples were filled into quartz glass capillaries (6

[*] Corresponding author: hoyer@physik.tu-chemnitz.de

mm diameter and 0.2 mm wall thickness) and sealed under vacuum. The incident wavelength of neutrons was 1.11 Å. The measurements have been performed in the Q-range between 0.4 $Å^{-1}$ and 10.4 $Å^{-1}$. Structure factors were obtained from the scattering intensities after absorption and inelasticity corrections and normalization to a vanadium standard, which were done with the CORRECT program described in [17].

X-ray diffraction experiments were carried out at the BW5 experimental station [18] at HASYLAB, DESY. The samples were filled and sealed into quartz capillaries of 2 mm in diameter and with wall thickness of about 0.02 mm. The energy of the radiation was 125 keV. The scattered intensity was measured between 0.4 $Å^{-1}$ and 20 $Å^{-1}$ with the scanning step ΔQ = 0.04 $Å^{-1}$. Statistical error at the tail of curve was less than 0.2%. Raw data were corrected for detector dead-time, background, polarization, absorption, and variations in detector solid angle.

3. Reverse Monte Carlo simulations

It has been illustrated in a number of studies that RMC [15] is a useful tool for modelling of the atomic structure of non-crystalline substances and determination of the partial pair correlation functions and other structural parameters (details of the technique one can find in a recent review [19]). Recently we have proven that reliable structure factors and partial pair correlation functions of a binary liquid alloy can be obtained with two independent diffraction curves if additional physical information (e.g. atomic size differences or coordination constraints) can be built in the simulations [20]. Due to different values of the X-ray atomic scattering factors ($f_{Ge}(0)$ = 32 e.u., $f_{Te}(0)$ = 52 e.u.) and the neutron scattering lengths (b_{Ge} = 8.185 fm, b_{Te} = 5.8 fm [21]) for Ge and Te and application of plausible physical constraints one may expect to get a reliable picture of the Ge-Te and Te-Te pair distribution functions.

Coupled simulations of the X-ray and neutron diffraction measurements were carried out with boxes of 15000 - 20000 atoms. The density in the amorphous state was taken to be 0.0282 $Å^{-3}$ [22].The densities of liquid $Ge_{15}Te_{85}$ were taken from [7]. The minimum distances between Te-Te, Te-Ge and Ge-Ge pairs were 2.5, 2.3 and 3.5 Å, respectively. In the amorphous state one Ge atom could have 3, 4 or 5 Te neighbours and Te atoms were forced to have either 1 or 2 Te neighbours (the detailed study of the amorphous $Ge_{15}Te_{85}$ one can find in [23]).

4. Results and discussion

The experimental structure factors of the amorphous and liquid $Ge_{15}Te_{85}$ are shown in Fig. 1. As an example, the simulated total structure factors for amorphous alloy are plotted there. The experimental data have been simulated with a similar quality for all temperatures in the liquid state.

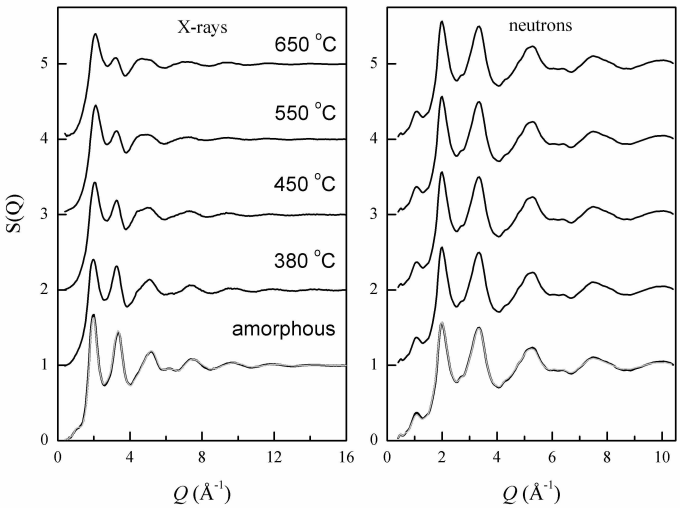

Fig. 1. The experimental (*black*) and RMC simulated (*light*) structure factors of amorphous and liquid $Ge_{15}Te_{85}$.

The partial structure factors and pair distribution functions of the amorphous and liquid alloys obtained with RMC are presented in Fig. 2 and the partial coordination parameters are given in Table 1. It should however be noted that the weight of the Ge-Ge partial structure factor is so small for $Ge_{15}Te_{85}$ composition that the diffraction measurements are not conclusive concerning the Ge-Ge pair distributions.

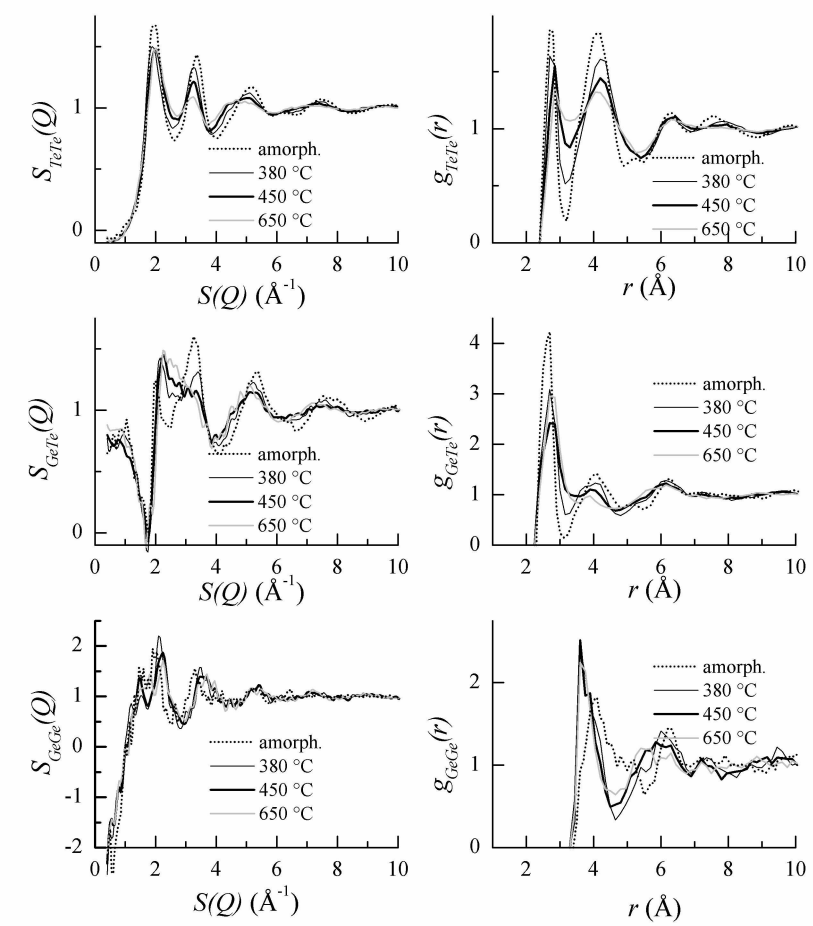

Fig. 2. Partial structure factors and pair correlation functions of amorphous and liquid $Ge_{15}Te_{85}$.

The partial structure factors and pair distribution functions are strongly temperature dependent (Fig. 2). In the amorphous state and in the liquid state close to the melting temperature (T_m = 375 °C) both $g_{TeTe}(r)$ and $g_{GeTe}(r)$ have a distinct first minimum. With increasing temperature the overlap between the first and second coordination spheres in $g_{TeTe}(r)$ and $g_{GeTe}(r)$ becomes stronger. It can be also observed from Table 1 that structural transformations of the eutectic $Ge_{15}Te_{85}$ alloy under heating are related with changes both in Te-Te and Ge-Te pairs.

Table 1. Bond lengths r and coordination numbers N for amorphous and liquid $Ge_{15}Te_{85}$.

Temperature	r_{TeTe} (Å)	r_{GeTe} (Å)	N_{TeTe}	N_{GeTe}	N_{TeX}
Amorphous	2.72	2.62	1.71	3.63	2.35
380 °C	2.75	2.7	1.7	3.7	2.35
450 °C	2.85	2.77	1.9	4.0	2.6
550 °C	2.88	2.82	1.9	4.0	2.6
650 °C	2.83	2.77	1.9	4.6	2.7

It is also seen (Fig. 2, Table 1) that the temperature induced structural changes in liquid $Ge_{15}Te_{85}$ are very pronounced in the temperature interval from the eutectic temperature up to 450 °C and they are not so strong at higher temperatures. This agrees with the temperature behaviour of the physico-chemical properties mentioned in Introduction.

The X-ray structure factor of the amorphous $Ge_{15}Te_{85}$ and the neutron structure factors of amorphous and liquid alloy near the melting point have a characteristic feature – the prepeak at about 1.05 Å. As the prepeak has much smaller amplitude for the X-ray case it can be assumed that this feature is connected to Ge-Te or Ge-Ge correlations, which have a larger contribution to the neutron scattering pattern. Analysis of the origin of prepeak in amorphous $Ge_{15}Te_{85}$ [23] has revealed that the prepeak is a consequence of enhanced Ge-Te and Ge-Ge correlations in the 1st - 3rd coordination shells.

Fig. 3 shows changes of the medium range order in amorphous and liquid $Ge_{15}Te_{85}$. The medium range Ge-Te and correlations in the amorphous sample reach up to 25 $Å^{-1}$. The medium range order is partly preserved in the liquid state close to the melting point and vanishes at elevated temperatures.

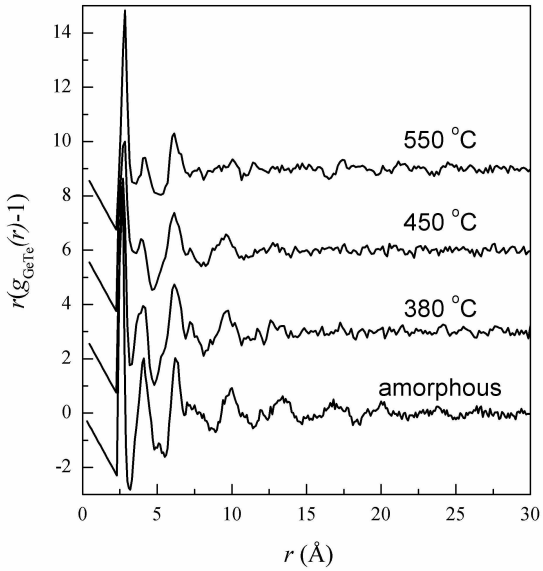

Fig. 7. Change of the medium range order in amorphous and liquid $Ge_{15}Te_{85}$.

5. Conclusions

Due to simultaneous reverse Monte Carlo simulations of the X-ray and neutron diffraction data for amorphous and liquid $Ge_{15}Te_{85}$ alloy the partial pair correlation functions and coordination parameters have been obtained. Analysis of these data has revealed that there exist similarities between the amorphous and liquid structure near the melting temperature. It is also established that in accordance with the physical properties the temperature induced structural changes in liquid $Ge_{15}Te_{85}$ are more pronounced close to the melting point. The structural transformations under heating are related with changes both in $g_{TeTe}(r)$ and $g_{GeTe}(r)$**.** The medium range Ge-Te correlations in the amorphous sample reach up to 25 $Å^{-1}$ and they are partly preserved in the liquid state up to 450 °C.

Acknowledgements

This work has been supported by the European Community-Access to Research Infrastructure action of the Improving Human Potential Programme, contract N° HPRI-CT 2001-00127. P.J. was supported by the OTKA (Hungarian Basic Research Found) grant N° T048580.

References

[1] H.-U. Tschirner, I. P. Pazdrij, R. Weikart, Wiss. Z. d. Techn. Hochsch. Karl-Marx-Stadt **25/2**, 219 (1983).
[2] H.-U. Tschirner, Th. Born, H. Neumann, W. Hoyer, M. Wobst, Wiss. Z. d. Techn. Hochsch. Karl-Marx-Stadt **28/2**, 249 (1986).
[3] F. Herwig, M. Wobst, Z. Metallkd. **82**, 917 (1991).
[4] Y. Tsuchiya, J. Non-Cryst. Solids **156-158**, 704 (1993).
[5] Y. Tsuchiya, J. Non-Cryst. Solids **312-314**, 212 (2002).
[6] H. Neumann, W. Matz, W. Hoyer, M. Wobst, Phys. Stat. Sol. A **90**, 489 (1985).
[7] C. Bergman, C. Bichara, J. P. Gaspard, Y. Tsuchiya, Phys. Rev. B **67**, 104202 (2003).
[8] S. R. Ovshinsky, Phys. Rev. Lett. **21**, 1450 (1968).
[9] J. Feinleib, J. de Neufville, S. C. Moss, S. R. Ovshinsky, Appl. Phys. Lett. **18**, 254 (1971).
[10] E. Nicotera, M. Corchia, G. De Giorgi, F. Villa, M. Antonini, J. Non-Cryst. Solids **11**, 417(1973).
[11] Y. Kameda, O. Uemura, T. Usuki, Mater. Trans. JIM **37**, 1655 (1996).
[12] O. Uemura, N. Hayasaka, S. Tokairin, T. Usuki, J. Non-Cryst. Solids **205-207**, 189 (1996).
[13] M. Sakurai, F. Kakinuma, E. Matsubara, K. Suzuki, J. Non-Cryst. Solids **312-314**, 585, (2002).
[14] K. Ichikawa, Y. Kameda, Q. Xu, M. Misawa, J. Non-Cryst. Solids **95-96**, 185 (1987).
[15] R. L. McGreevy, L. Pusztai, Mol. Simul. **1**, 359 (1988).
[16] A. Wannberg, A. Mellergård, P. Zetterström, R. Delaplane, M. Grönros, L-.E. Karlsson, R. L. McGreevy, J. Neutron Res. **8**, 133 (1999).
[17] M. A. Howe, R. L. McGreevy, P. Zetterström, CORRECT: A correction program for neutron diffraction data (NFL Studsvik internal report, 1996), ftp://www.studsvik.uu.se/pub/correct/
[18] H. Poulsen, J. Neuefeind, H. B. Neumann, J. R. Schneider, M. D. Zeidler J. Non-Cryst. Solids **188**, 63 (1995).
[19] R. L. McGreevy, J. Phys.: Condens. Matter **13**, R877 (2001).
[20] I. Kaban, S. Gruner, W. Hoyer, P. Jóvári, R. G. Delaplane, A. Wannberg, Presented at the 12th International Conference on Liquid and Amorphous Metals (LAM 12), 11-16 July, 2004, Metz, France (to be published in JNCS).
[21] V. F. Sears, Neutron News **3**, 26 (1992).
[22] F. Betts, A. Bienenstock, D. T. Keating, J. P. de Neufville, J. Non-Cryst. Solids **7**, 417 (1972).
[23] P. Jóvári, I. Kaban, W. Hoyer, R. G. Delaplane, A. Wannberg, J. Phys.: Condens. Matter **17**, 1529 (2005).