

## A structural study of liquid Te-rich Si-Te alloys

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**Abstract.** X-ray diffraction measurements using synchrotron radiation on liquid  $\text{Si}_x\text{Te}_{1-x}$  ( $x \leq 0.2$ ) were carried out at several temperatures. At constant temperature, the first peak, which is composed of Si-Te and Te-Te correlations, of the pair distribution function gradually shifts to the shorter distances with increasing Si content. These shifts indicate the substitution of Si-Te bond for the Te-Te bonds in the first peak. The total coordination number shows little temperature variation and remains about two in the temperature interval of a few hundreds of degrees. The composition and temperature behaviour of the Te-rich side of Si-Te liquid alloys has already been investigated, among which thermodynamic behaviour is a quite contrast to that of the Ge-Te alloys in the overlapping composition-temperature range of the present investigation. We clarify the evolution of the local structure of the liquid Si-Te alloys in comparison with the liquid Ge-Te alloys.

### 1. Introduction

Liquid Te-rich alloys exhibit unique temperature dependence of the physical properties [1, 2]. The thermodynamic susceptibilities (specific heat, isothermal compressibility and thermal expansion coefficient) for liquid  $\text{Ge}_{15}\text{Te}_{85}$  which is the eutectic alloy show the sharpest extremum so far found for liquid semiconductors [3, 4]. It has been clarified that the anomalous thermodynamic behaviour is a sign of the steep structural changes in the liquid with temperature [5].

Si and Ge belong to the 14<sup>th</sup> family of the periodic table and it is assumed that the liquid Si-Te alloy at the Te-rich side has the similar covalent bonding mechanism to the liquid Te-rich Ge-Te alloy and both physico-chemical properties would be much the same. The presumptions are in evidence in some experiments. The electrical conductivity of liquid Te-rich Si-Te alloy has a temperature dependence of a type of a liquid semiconductor [6]. The specific heat, compressibility and thermal expansion coefficient show an extremum in the temperature domain where the electrical transport properties change from semi-conductive to weak metallic state. The composition and temperature behaviour of the Te-rich side of Si-Te liquid alloys is a quite contrast to that of the Ge-Te alloys in the overlapping composition-temperature range, however. For example, the peak value of the specific heat and the



amount of volume contraction with temperature of  $\text{Si}_{15}\text{Te}_{85}$  are, respectively, about half and 1/3 of those of  $\text{Ge}_{15}\text{Te}_{85}$ , while their temperature variation takes place over much wider range. In other words the rate of structural changes with temperature in the Si-Te alloy is about halftimes as large as the one in the Ge-Te alloy.

In the present study we clarify the evolution of the local structure of the liquid Si-Te alloys in comparison with the liquid Ge-Te alloys.

## 2. Experimental

The Si-Te alloy samples were made from Si and Te shots of purity (99.999%) by direct mixing. The raw materials were sealed in a molten quartz tube in 3 mm diameter with 0.5 mm wall thickness under a vacuum of  $2 \times 10^{-6}$  Torr, and kept at 1243 K for 24 hours. The liquid alloy was shaken a few times during heating to make thorough mixing. After heating, the sample was quenched in iced water, and then the alloy was ground to grains. Finally the powder sample was encapsulated in a silica glass capillary in 2 mm diameter with 0.02 mm wall thickness for measurements under a vacuum of  $2 \times 10^{-6}$  Torr.

X-ray diffraction experiments were carried out with the angle dispersive method at the BL04B2 beam line [7] of the SPring-8, Japan. Incident photon energy was 113 keV obtained by the third harmonics reflection of Si(111) monochromator. The structure factor,  $F(q)$ , where  $q = 4\pi\sin\theta/\lambda$ ,  $2\theta$  is the diffraction angle, and  $\lambda$  the X-ray wavelength, was obtained from the net scattering intensities from the sample after standard corrections for the background and empty cell intensities, absorption and polarization [7, 8]. The measured temperatures were 763 K, 873 K, 923 K and 973 K for  $\text{Si}_x\text{Te}_{1-x}$  with  $x = 0.05, 0.10, \text{ and } 0.15$ , 873 K, 923K and 973 K for  $\text{Si}_{0.2}\text{Te}_{0.8}$ .

## 3. Results and Discussion

Figure 1 shows the structure factors,  $F(q)$ , for  $\text{Si}_x\text{Te}_{1-x}$  alloys at 873 K. It can be seen that the profile of  $F(q)$  changes systematically with Si concentration. With increasing Si concentration, the first peak shifts to smaller value of  $q$ , while the second peak to the larger value. The second peak height increases and the first minimum becomes deeper. A small hump, which is the indication of the development of the medium range order, appears around  $q = 0.8 \text{ \AA}^{-1}$  in  $F(q)$  for  $x = 0.15$  and  $0.2$ .

The total pair distribution function,  $g(r)$ , is obtained from the Fourier transform of  $F(q)$  [8],

$$g(r) = 1 + \frac{1}{2\pi^2 \rho r} \int (F(q) - 1) q \sin qrdq, \quad (1)$$

where  $\rho$  is the average number density of atoms in the alloy. The values of  $\rho$  used in this analysis are calculated using the molar volume data in [9]. Figure 2 shows the total pair distribution functions of  $\text{Si}_x\text{Te}_{1-x}$  alloys at 873 K. With increasing Si concentration very large changes in  $g(r)$  appear up the second peak. The first peak position shifts to the shorter distance from 2.86 Å for  $x = 0.05$  to 2.75 Å for  $x = 0.2$ , accompanying the decrease in the height. The second peak grows steeply and becomes prominent beyond  $x = 0.15$  while its position remains almost unchanged. Corresponding to the appearance of hump in  $F(q)$  around  $q = 0.8 \text{ \AA}^{-1}$  a new peak becomes apparent in around 7.8 Å in  $g(r)$ .

For a Si-Te alloy, the total structure factor,  $F(q)$ , is given by equation (2) in terms of Si-Si, Si-Te, Te-Si and Te-Te partial structure factors,  $F_{ij}(q)$ .

$$F(q) = w_{\text{SiSi}}(q)F_{\text{SiSi}}(q) + w_{\text{SiTe}}(q)F_{\text{SiTe}}(q) + w_{\text{TeSi}}(q)F_{\text{TeSi}}(q) + w_{\text{TeTe}}(q)F_{\text{TeTe}}(q), \quad (2)$$

where  $w_{ij}(q) = x_i x_j f_i(q) f_j(q) / (x_i f_i(q) + x_j f_j(q))^2$  in which  $f_i(q)$  and  $x_i$  are, respectively, the atomic form factor and the concentration of Si or Te. Since the  $q$ -dependence of  $w_{ij}(q)$  is weak, the total pair distribution function,  $g(r)$ , obtained by putting equation (2) into equation (1), can be approximated to equation (3) to a good approximation.

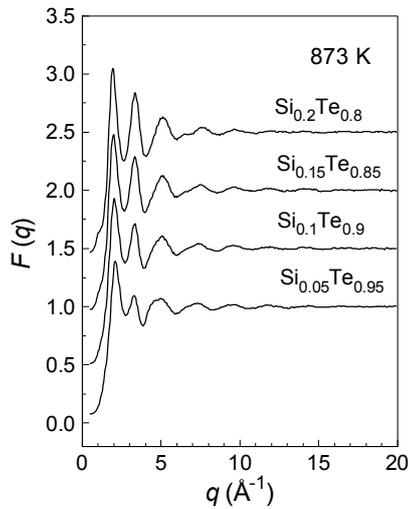


Figure 1. The structure factors for liquid  $\text{Si}_x\text{Te}_{1-x}$  alloys. The curves for  $\text{Si}_{0.1}\text{Te}_{0.9}$ ,  $\text{Si}_{0.15}\text{Te}_{0.85}$  and  $\text{Si}_{0.2}\text{Te}_{0.8}$  are shifted 0.5, 1.0 and 1.5, respectively.

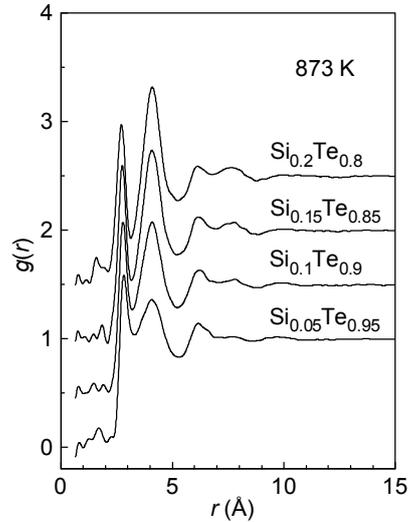


Figure 2. The total pair distribution functions for liquid Si-Te alloys. The curves for  $\text{Si}_{0.1}\text{Te}_{0.9}$ ,  $\text{Si}_{0.15}\text{Te}_{0.85}$  and  $\text{Si}_{0.2}\text{Te}_{0.8}$  are shifted 0.5, 1.0 and 1.5, respectively.

$$g(r) \approx c_{\text{SiSi}}g_{\text{SiSi}}(r) + c_{\text{SiTe}}g_{\text{SiTe}}(r) + c_{\text{TeSi}}g_{\text{TeSi}}(r) + c_{\text{TeTe}}g_{\text{TeTe}}(r), \quad (3)$$

where the total pair distribution function is a weighted sum of the four partial distribution functions,  $g_{ij}(r)$ , of Si-Si, Si-Te, Te-Si and Te-Te pairs, defined by equation (4). The weighting factors  $c_{ij}$  are  $x_i x_j Z_i Z_j / (x_i Z_i + x_j Z_j)^2$  with the atomic number of an atom  $i$ ,  $Z_i$ . The partial pair distribution function for an  $i$ - $j$  atom pair is the probability to find  $j$  atoms at the distance  $r$  when an  $i$  atom is at the origin.

$$g_{ij}(r) = 1 + \frac{1}{2\pi^2 \rho r} \int (F_{ij}(q) - 1) q \sin qr dq \quad (4)$$

Intuitive insight to the structure of liquid Si-Te alloy may be obtained from the total coordination numbers  $n$  for the definite peaks in the radial distribution function  $G(r) = 4\pi r^2 \rho g(r)$ .

$$n = \int_{r_1}^{r_2} G(r) dr \approx (c_{\text{SiSi}} + c_{\text{SiTe}}) n_{\text{Si}} + (c_{\text{TeSi}} + c_{\text{TeTe}}) n_{\text{Te}} \quad (5)$$

For the total coordination number,  $r_1$  and  $r_2$  were chosen to be 2.2 Å and the first minimum position of  $G(r)$ , respectively. The results are listed in table 1. The total coordination number remains about two though a slightly decreasing tendency with increasing Si fraction can be seen. Further the depth of the first minimum in  $g(r)$  becomes deeper as can be seen in figure 2, which indicates that overlap between the first and second coordination shell decreases. Since the atomic number of Si and Te is 14 and 52, respectively, the weighting factors,  $c_{\text{SiSi}}$  and  $c_{\text{SiTe}}$ , for the partial radial distribution function of a Si atom at the origin are 0.00398 and 0.0591, respectively, for the Si-richest  $\text{Si}_{0.2}\text{Te}_{0.8}$  alloy. Therefore, the composition-temperature dependence of the coordination number around a Te atom,  $n_{\text{Te}}$ , dominates the present results.

The coordination number in pure Te at the melting temperature, 450 °C, is about 2.7, and decreases to about two in the deeply under cooled liquid state, which has been interpreted as a liquid-liquid crossover transition in liquid Te. At the melting point the transition is almost finished and liquid Te is in a high temperature form in which inter-chain bonding caused by bond defects in a chain structure brings about a local three-dimensional structure. By adding Si, the present results indicate that the local structure around Te transforms back to a chain structure. A Si-Te alloy in the composition range from  $x = 0.15$  to 0.25 easily forms bulk glass of which the structure is shown to be Te chains interconnected with Si atoms tetrahedrally coordinated to four Te atoms. The results are in good agreement of Refs. [10, 11]. The latter structure is the structural unit of  $\text{Si}_2\text{Te}_3$  that is the only

Table 1. The total coordination number of  $\text{Si}_x\text{Te}_{1-x}$  alloys.

	763 K	873 K	923 K	973 K
$\text{Si}_{0.05}\text{Te}_{0.95}$	2.00±0.02	2.21±0.02	2.17±0.02	2.13±0.02
$\text{Si}_{0.1}\text{Te}_{0.9}$	2.07±0.02	2.08±0.02	2.08±0.02	2.06±0.02
$\text{Si}_{0.15}\text{Te}_{0.85}$	1.95±0.02	1.96±0.02	1.98±0.02	2.02±0.02
$\text{Si}_{0.2}\text{Te}_{0.8}$	—	1.92±0.02	1.84±0.02	1.85±0.02

stable compound in the Si-Te alloy. It is supposed, therefore, that added Si atoms compensate bond defects in Te chains to form tetrahedral unit with surrounding four Te atoms, which would decrease bond defects in a liquid and change the electrical transport properties from the semi-metallic to semi-conductive state. The measurements by Gasser *et al* support this conjecture [6].

The structural evolution in the Si-Te system summarized above comparatively contrasts with the results for the Te rich Ge-Te system in harmony with the difference in the behaviour of thermodynamic susceptibilities. For example, the total coordination number of  $\text{GeTe}_6$  is as large as the one for pure Te and increases apparently with increasing temperature from 623 to 796 K [12]. The origin of liquid-liquid transitions in both systems might be somewhat different, therefore.

#### 4. Conclusion

The X-ray scattering measurements were performed for liquid  $\text{Si}_x\text{Te}_{1-x}$  alloys with  $x = 0.05, 0.1, 0.15$  and  $0.2$  at several temperatures. The total pair distribution functions for the liquid Si-Te alloys exhibit characteristic behaviour. The variation of the first minimum in the total pair distribution function with Si concentration suggests that the bond defects in liquid Te decreases with addition of Si, and Si atom connects four Te chains and forms the tetrahedral unit. The total coordination number obtained is about two and decreases with increasing Si concentration. The structure of liquid Te by addition of Si atoms transforms to a chain structure similar to that of liquid Se. The  $\text{Si}_{0.15}\text{Te}_{0.85}$  and  $\text{Si}_{0.2}\text{Te}_{0.8}$  alloys have a hump at around  $0.8 \text{ \AA}^{-1}$  in the structure factor, which suggests that the medium range order still remain around near the melting temperature.

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