Molar volume of IVb-chalcogenide alloys: Compound-forming effects and structural changes with volume contraction

Y. Tsuchiya[*]

Department of Physics, Faculty of Science, Niigata University, Ikarashi 2-8050, Niigata 950-21, Japan

Abstract

The molar volume of IVb-chalcogenide systems has been reviewed. Anomalies in the composition and temperature dependence of the molar volume of the melt can be attributed to associates corresponding to an equi-atomic compound and a 1:2 compound, respectively, having ionic and covalent character. The latter becomes unstable with rising temperature, which causes anomalous contraction of the volume. The instability may be related with the Peierls distortion mechanism in the p-bonded systems. © 1998 Elsevier Science B.V.

Keywords: Molar volume; IVb-chalcogenide system; Compound-forming effects; Volume contraction; Peierls distortion mechanism

1. Introduction

Despite many advances made during recent years in understanding the thermodynamic properties of strongly associated liquids, the behaviour of the molar volume remains almost unexamined. This is because for most alloys the molar volume changes rather monotonically with composition and it does not provide any useful information to phase-diagram calculations. However, recent systematic studies have revealed that the molar volume is a very sensitive probe to the chemical short-range order (CSRO) in the melt of chalcogenide alloys [1–3].

In this paper the experimental results on the IVb (Si, Ge, Sn, Pb)-chalcogenide (Se, Te) (denoted by M and X, respectively) systems measured by Thurn and

Ruska [4,5], and in our laboratory have been summarized [1,6–8]. The phase diagram of the M–Te systems is characterized by an equi-atomic solid compound, MTe, except for the Si–Te system in which the compound, Si_2Te_3, is formed [9]. In the case of the X–Se system, a 1:2 compound, MSe_2, is formed in the Ge– and Sn–Se systems in addition. The bonding character is mainly ionic in the MX compound and covalent in the MX_2 compound [10]. It is generally believed that the prominent glass-forming ability of alloys at the chalcogen side is closely related to the development of a covalent network structure associated with the MX_2 compound in the melt [11]. It is shown that the molar volume of the IVb-chalcogenide system shows systematic variation reflecting the bonding nature of liquid alloys in accord with the other physico-chemical properties. Discussion is given on the nature of CSRO in the molten IVb-chalcogenide alloys and the structural changes with rising temperature.

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*Corresponding author. Tel.: 81-25-262-6146; fax: 81-25-263-3961.

2. Experimental

There exist several techniques to measure the density or the molar volume of liquid metals and alloys. Each of these has its own limitation [12]. For the chalcogenide alloys, a difficulty arises from the very high vapour pressure of the chalcogen elements. The high energy gamma-ray attenuation method has the advantage that the specimen can be sealed in an ampoule with a small volume and thus preferential evaporation of the more volatile element and oxidation of a specimen can be kept as small as possible although the absolute magnitude of the volume itself cannot be determined.

The principle of the method is briefly described in [4]. The molar volume, V, may be evaluated from the linear gamma-ray attenuation coefficient, μ_{alloys}, of an alloy using the relations

$$V = \rho_{\text{alloy}}/(A_1 x_1 + A_2 x_2), \tag{1}$$

$$\rho_{\text{alloy}} = \mu_{\text{alloy}}^*/\mu_{\text{alloy}} \tag{2}$$

and

$$\mu_{\text{alloy}}^* = (\mu_1^* A_1 x_1 + \mu_2^* A_2 x_2)/(A_1 x_1 + A_2 x_2), \tag{3}$$

where ρ_{alloy} is the mass density of an alloy, μ_i^* the mass absorption coefficient, A_i the atomic mass, and x_i the fraction of an element i. The mass absorption coefficient is assumed to be independent of alloying and temperature. It can be determined by measurement on a bulk specimen or a powder compressed, for example in a cylindrical steel tube.

3. Summary of experimental results

The molar volumes of the IVb (Si, Ge, Sn, Pb)–Te systems at 1000°C are plotted as a function of Te fraction in Fig. 1 [1,5–7]. Since the melting point of Si ($T_m=1414°C$) is beyond the accessible temperature for the present experiments, the results only in the Te-rich region were available. The excess mixing volume, ΔV_m, is shown in Fig. 2. In going from Ge to Pb, a maximum in ΔV_m shifts to 50 at.% Te and it grows to a sharp peak in the Pb–Te system. It has been shown that the gross feature of ΔV_m around 50 at.% is insensitive to the variation in temperature [6,7]. In
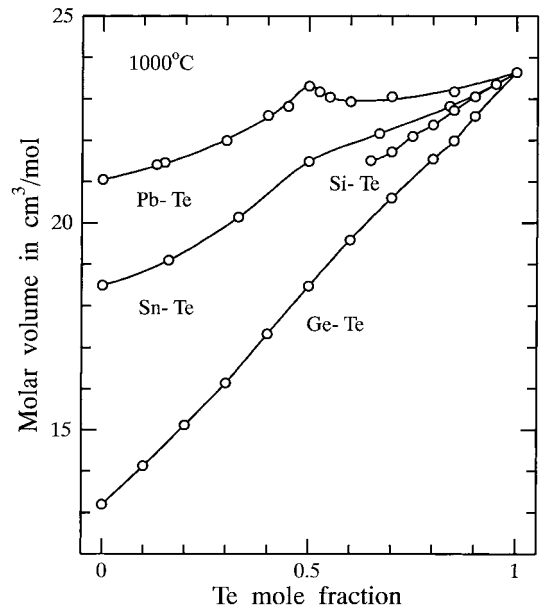

Fig. 1. Molar volume of IVb (Si, Ge, Sn, Pb)–Te alloys at 1000°C. The lines are drawn as a guide for the eye.
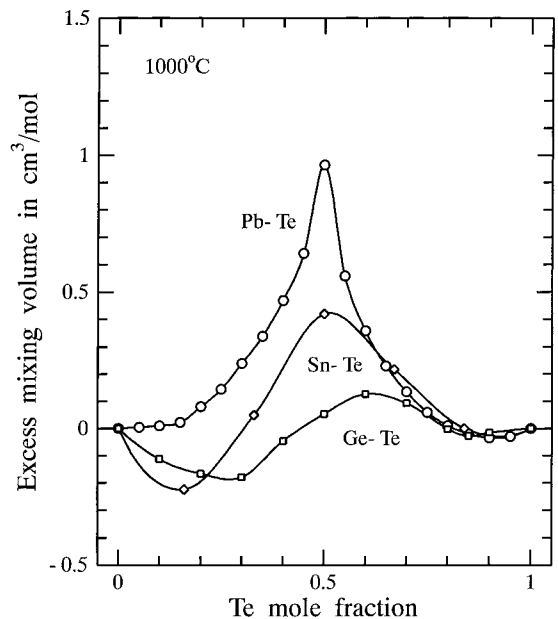

Fig. 2. Excess mixing volume of IVb (Ge, Sn, Pb)–Te alloys at 1000°C. The lines are drawn as a guide for the eye.
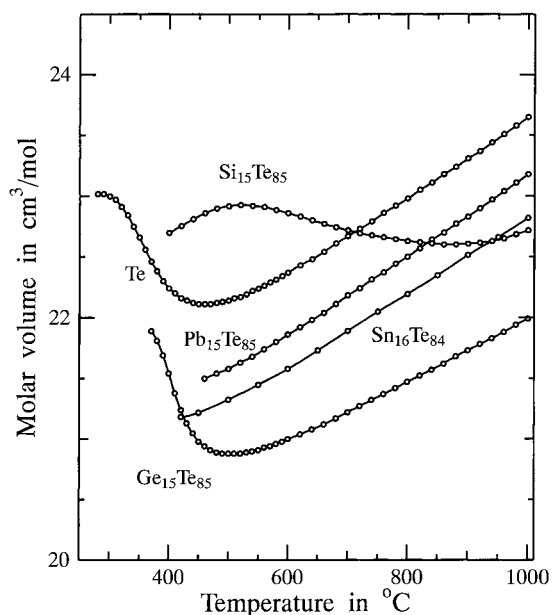
Fig. 3. Molar volume of Te and IVb (Si, Ge, Sn, Pb)–Te alloys around 15 at.% as a function of temperature. The lines are drawn as a guide for the eye.
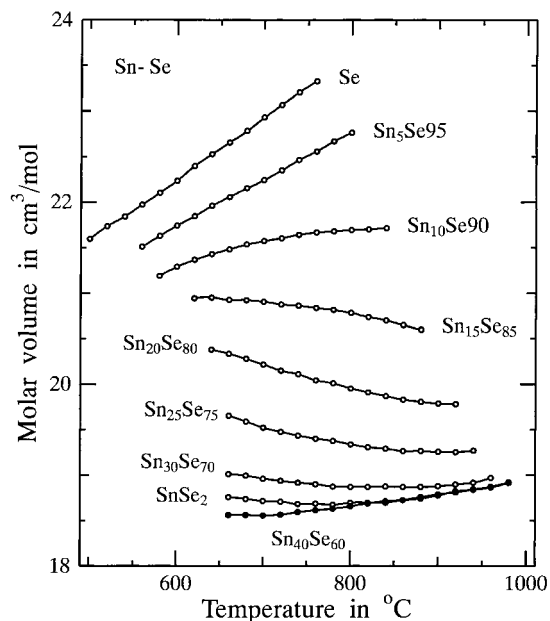

Fig. 4. Molar volume of Sn–Te alloys at the Se-rich side. The lines are drawn as a guide for the eye.

contrast, the molar volume of the Si–Te and Ge–Te systems at low temperatures has a very complex composition-dependence, which has its origin in the anomalous volume contraction occurring in Te-rich alloys as plotted in Fig. 3 for alloys around 15 at.% Te and pure Te.

A similar volume contraction occurs at much higher temperatures in the Ge–Se and Sn–Se systems as plotted for Sn–Se alloys in Fig. 4 [5,8]. The molar volume of liquid Se increases almost linearly in this temperature range. Alloying Ge or Sn into Se brings about non-linear temperature dependence and in fact the volume contracts with rising temperature to high levels. The region where the volume contracts shifts to lower temperatures with increasing Ge or Sn fraction. At the Ge or Sn side, the two-melt region appears, of which the consolute temperature is higher than 900°C [13,14] and volume data are available for the Sn–Se alloy in a limited temperature range only. Reflecting the contraction, ΔV_m at the Se side shows very large temperature dependence as plotted in Fig. 5. A local maximum develops around the $GeSe_2$ at low temperatures. It is also noted that a small but definite cusp-like maximum appears at 50 at.% in the Sn–Se system.
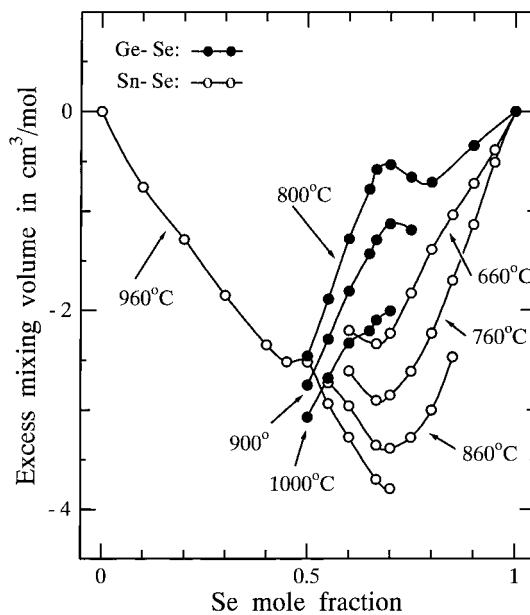

Fig. 5. Excess mixing volume of Ge– and Sn–Te alloys at several temperatures. The lines are drawn as a guide for the eye.

4. Discussion

Anomalous physico-chemical properties of the molten alloy are generally correlated with the existence of definite compounds in the phase diagram. It is believed that a CSRO originating from the equiatomic solid compound dominates the thermodynamic properties of the IVb-chalcogenide systems. For example, the mixing enthalpy of the IVb–Te system has been adequately reproduced with an associated model assuming an associate of a type, MTe [15,16]. It has also been shown that an additional associate, MSe_2, has only minor effects as far as the heat of mixing of the Sn–Se system is concerned [16].

The MTe compound takes an NaCl-type rather open structure of which the volume is larger than an average of the volume of the constituents except for the Ge–Te system [17]. The positive ΔV_m of the IVb–Te system may, therefore, indicate that significant changes in local ionic arrangement do not take place upon melting and ionic bonding is preserved in the liquid state. In ordered ionic molten alloys, each ionic species surrounds itself as much as possible with ions of the opposite sign. Thus the coordination number increases away from stoichiometry while the bond length remains almost unchanged, causing an increase in density or a decrease in volume on either side of the compound composition [10]. Thus the sharpness of the peak in the excess volume would more or less reflect the stability of associate in the melt. The results for the M–Te system shown in Fig. 2 suggest that the associates in the Pb–Te system are most stable in agreement with the results of the mixing enthalpy [16,17]. In this respect, a small cusp persisting in ΔV_m for the Sn–Se system in Fig. 5 is worth noting. It suggests that a CSRO in the SN–Se melt around 50 at.% has an ionic character to some extent.

As seen in Fig. 5, ΔV_m for the Sn–Se system has a pronounced minimum around 70 at.% Se which becomes shallow with decreasing temperature. The results might be ascribed to the formation of associates such as $SnSe_2$. Recent MD calculations suggest that an off-stoichiometric alloy of the Se-based molten binary system at the Se side is composed of metal–Se clusters and additional Se atoms to a rough approximation [18]. The latter have the tendency to form chain molecules and the atomic volume of a Se atom in chain molecules is much larger than the one in metal–Se clusters. In the composition region where the fraction of Se exceeds a value, $x_c = Z/(1 + Z)$, where Z is the coordination number of a metallic atom, the tendency of Se atoms to form chain molecules will become more and more appreciable with increasing Se fraction and thus the molar volume would very rapidly increase to the Se value. Consequently, a minimum in ΔV_m is expected to appear around x_c which is not so much dependent on the kind of metallic element. Thus the minimum in ΔV_m is not directly related to compound formation in the molten M–Se system. The presumption agrees well with the experimental results so far reported [19,20].

Another characteristic feature of the molar volume of IVb-chalcogenide systems is the non-linear temperature dependence which appears at the chalcogenide side. Actually the volume contracts with rising temperature as seen in Figs. 3 and 4. A similar anomalous volume contraction has been found in the supercooled Te as also plotted in Fig. 3. For Te, the volume contraction corresponds to the structural change from a low- to a high-temperature form [21]. They are, respectively, characterized by the coordination number $Z = 2$ and $Z \sim 3$ [22]. The volume expansion coefficient, $V^{-1} (dV/dT)$, takes a negative minimum at which the rate of volume contraction with rising temperature becomes largest. Fig. 6 shows the position of the minimum, T^*, as a function of composition. Assuming the structural change from a low- to a high-temperature form for chalcogenide alloys as well, the physical meaning of T^* is a temperature at which the structural change has proceeded about half way to a high-temperature form and thus gives a measure of stability to associates involved in the structural changes.

The microscopic origin of this structural change appears to be still open, though quite often it is ascribed to the thermal dissociation of a network structure [4]. For Se and Te, on the other hand, the structural changes are induced by forming a network structure with rising temperature [22]. Thus if a small amount of Ge is added to Te, for example, a network structure would be more easily formed and the volume contraction would take place at much lower temperatures than in pure Te. The experimental results for Te-based alloys, however, are in the other way as shown in Figs. 3 and 6.
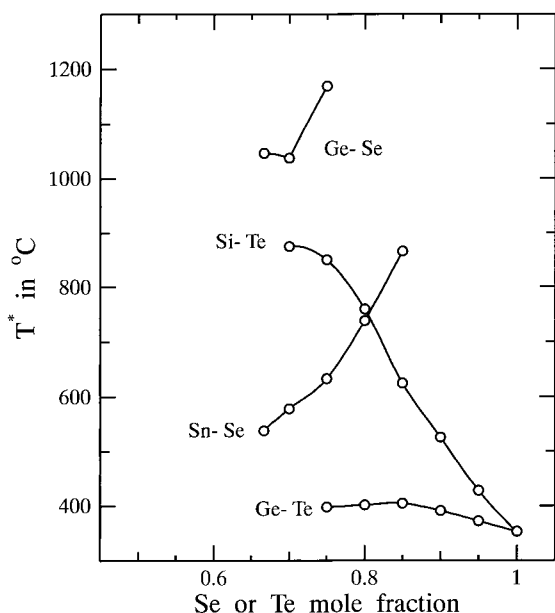
Fig. 6. The temperature, T^*, at which the thermal expansion coefficient takes a negative minimum. The lines are drawn as a guide for the eye.

Table 1
Possible atomic association in molten IVb-chalcogenide systems. MX compounds have basically ionic characters. Covalent network structures originated from MX_2 and related compounds in square brackets develop at low temperatures and show rapid structural changes with rising temperatures

	Si	Ge	Sn	Pb
Se	$[SiSe_2]$	$GeSe$, $[GeSe_2]$	$SnSe$, $[SnSe_2]$	$PbSe$
Te	$[Si_2Te_3]$	$GeTe$, $[GeTe_2]$	$SnTe$,	$PbTe$

becomes unstable. If this is the case, a measure of the energy gain would be given by RT^* (R: the gas constant) in terms of T^* plotted in Fig. 6 and it is not in contradiction with a value expected [24–26].

The possible atomic associates in IVb-chalcogenide systems and their stability inferred from the present study together with other various properties are summarized in Table 1. Since diffraction experiments suggest that a CSRO similar to $GeSe_2$ develops in a glassy Ge–Te alloy, $GeTe_2$ is listed for the Ge–Te system [10], though no solid compound corresponding to $GeTe_2$ is found in the phase diagram. As the atomic number of both IVb and chalcogen elements increases, a tendency to form MX compound with ionic bonding increases and in contrast a tendency to form a covalent network structure based on MX_2 or related compound decreases. This is in good accord with the general bonding feature found for compound semiconductors [10,23].

From an elementary point of view, the existence of strong heteroatomic interaction should be in favour of a negative ΔV_m, and a model emphasizing a close correlation between ΔV_m and mixing enthalpy has been proposed. From the Ge– to Pb–Te system, however, ΔV_m grows to a sharp peak while the mixing enthalpy becomes more negative [16]. Moreover, for the Me–Se system no such pronounced peak is found in ΔV_m though the magnitude of the mixing enthalpy is much larger as compared with the corresponding telluride [16]. So the general relation proposed in [27] does not hold for the IVb-chalcogenide system. On the other hand there exist quantitative relations among specific heat, compressibility and thermal expansion coefficient as a function of temperature. In the case that rapid structural changes occur as found in the present case, these quantities involve the contribution associated with the rate of structural changes with rising temperature or with an applied pressure. It has

In the solid binary semiconducting alloys, it is well known that a Peierls distortion in the p-bonding mechanism plays an essential role in the stability of covalent structures [23]. Gaspard et al. have shown that periodicity is not a necessary condition for the Peierls distortion mechanism and thus it can be responsible for the stability of a local structural arrangement in amorphous and liquid materials [24]. It is also suggested that the Peierls distorted structure has a lower density than the undistorted one. Recent MD calculations have shown that the Peierls distortion mechanism indeed stabilizes the chain structure of liquid Te at low temperature [25]. With rising temperature, the entropic term exceeds an energy gain due to the Peierls distortion to result in a more isotropic and denser structure at high temperatures. Since it is difficult to expect that the nature of a structural transition suddenly changes by adding a small amount of Ge to Te, the Peierls distortion mechanism could be a plausible origin for network structures in molten IVb-chalcogenide alloys. The volume contraction occurs in the temperature region where the entropic term exceeds the energy gain due to the Peierls distortion and a covalent network structure

been predicted that excess contributions satisfy the Ehrenfest relations in an extended form [3,6], which has been confirmed, for example, by experimental results for pure Te [21] and $Ge_{15}Te_{85}$ [28].

5. Conclusions

The molar volume of the IVb-chalcogenide systems has been summarized. The compound-forming tendency becomes prominent either at 50 or around 66.6 at.% of chalcogen element. The equi-atomic compound having an ionic bonding character is stabilized in the melt of heavier elements, while the covalent network structure based on an MX_2 compound develops in an alloy of lighter elements. The latter becomes unstable with rising temperature to result in structural changes with large volume contraction. The Peierls distortion mechanism may explain the phenomenon.

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