Glass Forming Ability of GeTeSn with Tin Concentration and Initial Conditions

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Solid samples of $(Ge_{15}Te_{85})_{1-x}Sn_x$ and $(Sn_xGe_{1-x})_{15}Te_{85}$ ternary alloys with different tin concentrations were obtained from the liquid state at different initial temperatures (T_0) by the splat cooling technique. They were analized by X-ray diffraction and Mössbauer spectroscopy. The results were compared with results obtained in similar studies on slowly cooled and annealed samples. The previous observation that increasing tin concentration renders the formation of the amorphous phase more difficult, is confirmed. For a fixed x, and $T_0 < 800\,°C$, the higher T_0 the easier the glassy phase is obtained. This behaviour reverses for $T_0 > 800\,°C$.

Introduction

In this work, which is complementary to another one concerning the alloy InTeSn [1], the influence of tin concentration on the formation of amorphous GeTeSn alloy is studied. In GeTeSn the Mössbauer active tin incorporates substitutionally. We also attempted to establish the relationship between the glass forming ability and the temperature of the melt from which the samples are quenched.

Experimental

$(Ge_{15}Te_{85})_{1-x}Sn_x$ was prepared by forming first $Ge_{15}Te_{85}$ (eut.) and then adding tin (x from 5.1 to 20.4 at.%), and $(Sn_xGe_{1-x})_{15}Te_{85}$ by forming first Sn_xGe_{1-x} with $x = 25.6$, 38 and 52.1 at.% and then adding Te. In all cases the material was heated at 1000 °C for 30 hs in a previously evacuated furnace under Ar. Samples with thickness between 30 and 60 μm were obtained with the splat cooling equipment described in [2]. This equipment has Cu pistons at room temperature; its cooling rate was 10^5-10^6 K/s. The samples were quenched from temperatures in the range 450–1100 °C and analized by Mössbauer spectroscopy (SnO_3Ba source at room temperature) and X-ray diffraction (Debye camera with Cu target).

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Results

The X-ray diffraction patterns of slowly cooled material show two crystalline phases, one of the Te and a second one that is changing according to the contents of Sn. The latter is similar to that of GeTe for low x values (rhombohedric with $a = 5.986$ Å and $\alpha = 88.35°$) and becomes cubic with increasing x in an expansion process leading to SnTe (cubic with $a = 6.303$ Å). The change in the lattice parameter with increasing x is shown in Table 1.

Table 1.

Tin concentration x (at.%)	7.7	10.2	15.3	20.4
Lattice parameter a (Å)	6.11	6.13	6.18	6.20

The Mössbauer spectra of slowly cooled samples consist of a single line with an Isomer Shift (IS) that grows with increasing tin concentration as is shown in Fig. 1 for both alloys.

The IS observed are characteristic of divalent tin compounds and suggest that the chemical bond is formed by p electrons. Regarding the electronic configuration of tin in a divalent compound as $5\,s^2\,p^z$ with $0 \leqq z \leqq 2$, the IS is determined by the occupation of the 5 p states [3]. According to Flinn [4], the relationship between the IS and the effective number of 5 s and 5 p electrons (n_s and n_p) in the bond for a stannous compound ($n = 2$) with a SnO_3Ba source at room temperature is

$$IS = 4.77 - 2.55\,n_p - 0.03\,n_p^2.$$

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In this way n_p changes from 0.66 to 0.55 when the IS goes from 3.07 to 3.36 mm/s, confirming the existence of an ionic-covalent bond for tin.

The increase of the IS with tin concentration is in agreement with the lattice expansion observed with X-rays. The effect of this expansion on tin is to favour the 5 s states relative to the 5 p ones, and thus to produce a net increase in the charge density at the nucleus.

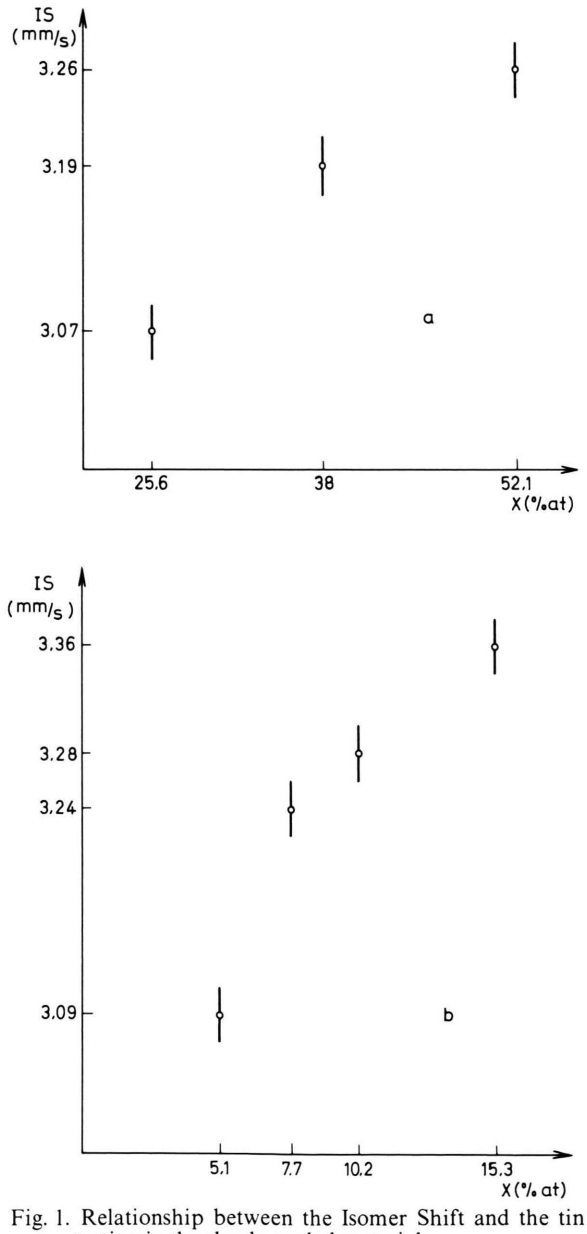

Fig. 1. Relationship between the Isomer Shift and the tin concentration in the slowly cooled material:
a) $(Sn_xGe_{1-x})_{15}Te_{85}$, b) $(Ge_{15}Te_{85})_{1-x}Sn_x$.

At the same time the line width decreases with increasing tin concentration, which is related to the change in the crystalline system. The larger line width for lower values of x suggests the existence of an electric field gradient in a rhombohedric lattice with tin in the sites of Ge for which the quadrupole splitting could not be resolved. When x grows, the structure becomes cubic, the quadrupole splitting approaches zero and the width decreases.

The material obtained by splat quenching with small tin concentrations (up to 7.7%) shows only amorphous phases when analized by X-ray diffraction. When x increases, a crystalline phase grows simultaneously with the amorphous structure. This new phase is similar to the cubic one observed when the material is slowly cooled. The amount of crystalline phase decreases with increasing initial temperature T_0 of the melt up to a certain temperature (about 800 °C). Above this temperature this behaviour reverses and in addition to the cubic phase, crystalline Te is seen. This can be explained by the fact that a memory effect appears in the fast cooling process. Above $T_0 = 800$ °C the SnTe and the GeTe bonds begin to break, so that there are more free Te atoms, and this remains effective when the material is rapidly quenched.

Quenched samples with T_0 between 450 and 1100 °C show two single line Mössbauer spectra. The first, with an IS between 2.00 and 2.25 mm/s, corresponds to tin in an amorphous phase; it disappears gradually when the alloy is annealed. This IS is interpreted as corresponding to neutral tin with an effective number of 5 s electrons in the range 1.07–1.18 for IS in the mentioned range. The different values of the IS of this peak could be correlated neither with tin concentrations nor with T_0. This suggests that there is not only one amorphous phase. This assumption was corroborated in some samples by the fact that the best adjustment could be obtained by supposing a quadrupole splitting with $Q = 0.75-0.80$ mm/s.

The second line is produced by tin in a crystalline phase that goes from the GeTe structure to the SnTe one when the tin concentration increases. The IS of this line changes from 3.20 to 3.45 mm/s indicating that the chemical bond of tin is similar to that observed in the slowly cooled material.

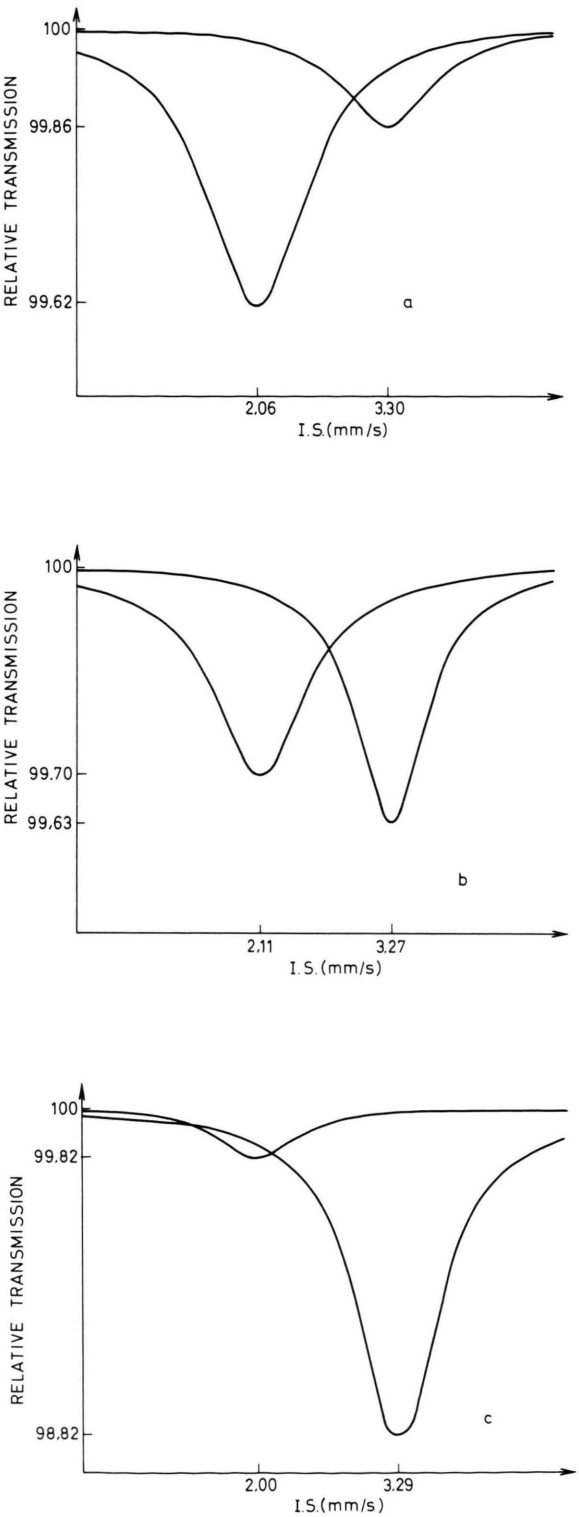

Fig. 2. Mössbauer spectra of the quenched samples: a) $Sn_{5.7}Ge_{9.3}Te_{85}$, b) $Sn_{7.8}Ge_{7.2}Te_{85}$, c) $Sn_{10.2}Ge_{13.5}Te_{76.3}$.

In agreement with the X-ray results, the absorption ratio between the first peak (amorphous phase) and the second one (crystalline phase) decreases when tin concentration becomes larger, as can be seen in Figure 2. This confirms that the addition of tin inhibits the formation of the amorphous phase.

On the other hand, the results obtained with GeTeSn differ from the ones for InTeSn [1] by the fact that for the former no systematic increase of the relative absorption of the amorphous phase line with T_0 was observed.

Finally, the annealing of the samples produced a gradual disappearance of the amorphous phase line with a corresponding increase of the crystalline phase one. After annealing for 30 hs at 300 °C the crystalline peak absorption is 5–10 times greater than that of the quenched samples and correspondingly greater than the peak of the amorphous phase, when fully recrystallization is achieved. This means that the amount of tin in the crystalline phase of the quenched samples is 5–10 times smaller than that of the amorphous phase. Also, this result points out that the "f" factor of the Mössbauer effect is 5–10 times smaller in the amorphous phase than in the crystalline phase.

As can be seen in Table 2, the IS of the annealed sample peak (IS_1) is smaller than the IS of the slowly cooled sample peak (IS_2), and both are smaller than the IS of the quenched sample crystalline peak (IS_3). IS_1 grows with tin concentration in a similar way as IS_2 due to the reasons explained before. This behaviour could not be seen in IS_3.

The systematic relationship between IS_1 and IS_2 ($IS_1 < IS_2$) could be explained in the following way: the crystalline lattice that produces IS_3 resembles the SnTe one more than that wich produces IS_2. So the proportion between tin and Ge is greater in the crystalline phase of the quenched samples than in the slowly cooled sample. This means that this proportion is greater in the crystalline phase of the quenched samples than in the amorphous

Table 2.

	IS_1 (mm/s)	IS_2 (mm/s)	IS_3 (mm/s)
$Sn_{5.1}Ge_{14.2}Te_{80.7}$	2.75	3.09	3.45
$Sn_{5.7}Ge_{9.3}Te_{85}$	2.96	3.19	3.30
$Sn_{7.8}Ge_{7.2}Te_{85}$	3.21	3.26	3.45

one. In this way, when the last recrystallizes, the resultant lattice resembles more the GeTe structure, with tin in sites of Ge, than the SnTe structure. This could be explained supposing that the liquid presents local fluctuations in concentration so that there would be places where SnTe is more abundant than the other component. These clusters, when solidified, become crystalline with a tin concentration greater than the mean value.

Conclusions

Like in the InTeSn alloys, an increase of tin concentration tends to inhibit the formation of amorphous phases. Evidently the high affinity between Sn and Te favours the formation of nucleation center for crystalline phases. On the other hand, with increasing T_0 the formation of amorphous phases is enhanced. This behaviour may be correlated with an increase with T_0 of the disorder in the liquid phase, a situation that is preserved when the sample is quenched. The beginning of dissociation above 800 °C produces an opposite tendency.

Acknowledgements

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