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## *Self-diffusion of Sn and Te in $Pb_{0.8}Sn_{0.2}Te$ at a temperature of 600° C*

$Pb_{1-x}Sn_xTe$ is a material of considerable interest for use in tunable laser diodes [1] and despite much work on material and device preparation very little information is available on self- and impurity-diffusion, although such data are important in the control of material and device parameters. Simirskii *et al.* [2] have described the results of radio-tracer Sn self-diffusion measurements (using Sn 113) in single-crystal samples with $x = 0.1$ and 0.2 at temperatures between 600 and 750° C, measured as a function of non-stoichiometry on the Te-rich side. A sealed silica ampoule arrangement requiring three separate temperature zones was used. However, according to Brebrick [3] a two-zone system is sufficient to define the degree of non-stoichiometry with the sample in the high-temperature zone and the temperature of the cooler zone used to control the non-stoichiometry. We have used such a two-zone system to measure the self-diffusivities of Sn 113 and Te 127 m in $Pb_{0.8}Sn_{0.2}Te$ at 600° C, over a range of Te partial pressures.

The diffusion samples were obtained from a single-crystal boule grown by a vapour-phase vertical Bridgman technique [1]. Samples with masses of approximately $1.5 \times 10^{-4}$ kg and thicknesses of about 1 mm were used. Dislocation densities were typically about $10^8$ m$^{-2}$. All samples were annealed for 10 days at 600° C in sealed silica ampoules with excess $Pb_{0.8}Sn_{0.2}Te$ prior to the self-diffusion experiments. Sample composition was confirmed by an electron beam microprobe. The principal faces of the samples were made parallel by lapping followed by a chemical polish using 4 vol% Br–HBr. All the radio-tracer diffusion experiments were carried out in sealed silica ampoules which had been acid etched ($HF/HNO_3$ etch) and vacuum baked at 1100° C prior to being loaded and sealed-off. The internal volume of the ampoule was approximately $6 \times 10^{-6}$ m$^3$. The diffusion source for each of the Sn 113 diffusions was $10^{-3}$ kg of granular $Pb_{0.8}Sn_{0.2}Te$ containing 1.2 MBq Sn 113. The Sn 113 source was held at the same temperature as the diffusion sample (600° C). The Te partial pressure, $P_{Te_2}$, was controlled by adding approximately $10^{-5}$ kg Te to the ampoule and varying the temperature (< 600° C) of the tip of the ampoule remote from the sample and source. In the Te 127 m diffusions the same procedures were followed except that 13.3 kPa of argon was admitted to the ampoule before it was sealed-off and the diffusion source was now also provided by the Te pellet used to control $P_{Te_2}$: the ampoule therefore contained only the diffusion sample and Te pellet (about 3 MBq Te 127 m). The argon pressure was needed to avoid surface deterioration of the sample during the diffusion anneal. For all the experiments the anneal period was 36 h. Radio-tracer diffusion profiles were obtained by standard radio-assay methods. All the profiles

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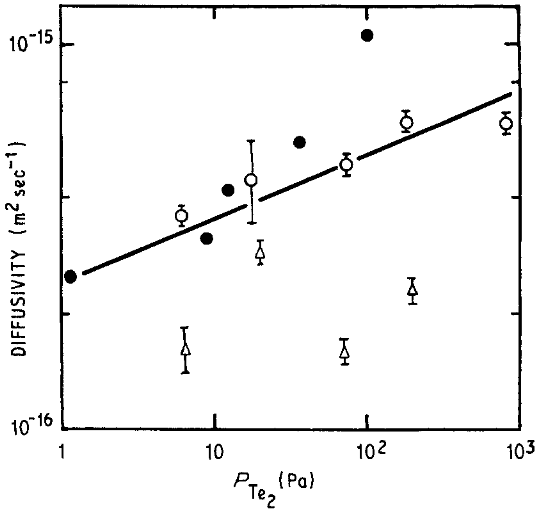

*Figure 1* ● (from [2]) and ○ show Sn 113 diffusivities; △ show Te 127 m diffusivities. The solid line represents a $P_{Te_2}^{1/6}$ dependence.

gave good fits to error-function dependence and the self-diffusivities were found using the method of Hall [4].

The Sn 113 was obtained by neutron irradiation of natural Sn so that Sb 125 was introduced as a radiochemical impurity amounting to approximately $1.5 \times 10^{18}$ atoms Sb 125 $kg^{-1}$ irradiated Sn. Simirskii *et al.* [2] removed the Sb 125 from their Sn before use. We did not attempt to do this as the Sb 125 concentration is far too small to affect the electrical properties in the sample [5]. Sn 113 was detected by its gamma emission at an energy of 0.39 MeV using a multi-channel analyser.

The experimental self-diffusivities are shown in Fig. 1 as a function of $P_{Te_2}$. Also shown are the Sn 113 data at 600° C from [2]. There is clearly good agreement between our results and those of [2] for Sn 113 diffusion. Not shown in Fig. 1 is a Sn 113 diffusivity of $(2.2 \pm 0.3) \times 10^{-16}\ m^2\ sec^{-1}$ obtained in the absence of any added Te. This result, together with those shown in Fig. 1, confirms that the non-stoichiometry of the sample and diffusion source is controlled by the added Te and also that the diffusion source is initially more metal-rich than the level corresponding to the lowest $P_{Te_2}$ shown in Fig. 1. Whereas, Simirskii *et al.* [2] concluded that the Sn self-diffusivity was proportional to $P_{Te_2}^{1/3}$, our data suggest a dependence closer to $P_{Te_2}^{1/6}$. For Te diffusion under saturated $P_{Te_2}$ at 600° C severe thermal etching of the sample surface prevented a diffusivity measurement being obtained. This problem was not found at the lower $P_{Te_2}$ values shown in Fig. 1 where the Te self-diffusivity shows a $P_{Te_2}^m$ dependence, where $|m| \lesssim \frac{1}{4}$. The recent literature on $Pb_{0.8}Sn_{0.2}Te$ [5], PbTe [6] and SnTe [6, 7] strongly suggests that the native acceptor is either a singly or doubly ionised metal vacancy, that is $V_M'$ or $V_M''$. Under Te-rich conditions the electro-neutrality condition (e.n.c.) at 600° C could then be either $p = 2[V_M'']$ or $p = [V_M']$, where $p$ is the free hole concentration. Table I summarizes the $m$ values which, through $P_{Te_2}^m$, give the concentration dependence of various native defects on $P_{Te_2}$ for each e.n.c. The self-diffusivities of Sn and Te will show the same $P_{Te_2}$ dependence as the defect involved in the diffusion process. For Sn diffusion an $m = \frac{1}{3}$ dependence uniquely fixes the e.n.c. as $p = 2[V_M'']$ and identifies $V_M'$ as the diffusing defect. If however $m = \frac{1}{6}$, $p = 2[V_M'']$ but the diffusing defect could be $V_M''$, $(V_M M_i)^{\cdot}$ or $(V_M V_{Te})^{\cdot}$, where $M_i$ is an interstitial defect. The Te diffusivities show too much scatter to enable the e.n.c. to be decided but taking $p = 2[V_M'']$ (from the Sn data) Te diffusion proceeds via $V_{Te}^{\cdot\cdot}$, $(V_M V_{Te})^{\cdot}$ or $(V_{Te} Te_i)^{\cdot}$, where $Te_i$ is an interstitial defect.

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TABLE I Summary of $m$ values for various native defects for each electro-neutrality condition

| Electro-neutrality condition | Defect | | | | | |
|---|---|---|---|---|---|---|
| | $V_M''$ | $V_M'$ | $V_{Te}^{\cdot\cdot}$ | $V_{Te}^{\cdot}$ | $(V_M M_i)^{\cdot}$<br>$(V_M V_{Te})^{\cdot}$ | $(V_M V_{Te})'$<br>$(V_{Te} V_i)^{\cdot}$ |
| $p = 2[V_M'']$ | $\frac{1}{6}$ | $\frac{1}{3}$ | $-\frac{1}{6}$ | $-\frac{1}{3}$ | $\frac{1}{6}$ | $-\frac{1}{6}$ |
| $p = [V_M']$ | 0 | $\frac{1}{4}$ | 0 | $-\frac{1}{4}$ | $\frac{1}{4}$ | $-\frac{1}{4}$ |

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## *Mechanical quality control of β-alumina membranes using acoustic emission*

Beta-alumina membranes are most usually used in the sodium–sulphur battery system as a solid electrolyte. The performance of this battery system strongly depends on the properties and quality of the solid electrolyte. Along with a high ionic conductivity, β-alumina membranes must have a high mechanical strength which is a prerequisite for a satisfactory cycle life.

Usually, the fracture strength of β-alumina membranes is determined from the mechanical load under which they break down [1–3]. The development of a non-destructive method of determination of the fracture strength would make it possible to perform screening tests prior to the incorporation of the solid electrolyte membrane in the cell.

The present paper presents a possible solution of the problem.

It is known [4–6] that the formation of microcracks and the widening of already existing ones leads to the release of energy as elastic waves. This process is known as acoustic emission (AE). The study of AE under mechanical loading of various materials may yield useful information on the existence of macroscopic defects in the structure and on the mechanical characteristics of the sample.

In our experiments we determined the fracture strength of β-alumina membranes with simultaneous recording of the AE.

The membranes were shaped like closed-end tubes with the following dimensions: outer diameter 9 mm, wall thickness 1.2 mm and length 70 mm. The membranes were prepared from the same starting materials under identical conditions. The density of the sintered samples was 3.20 g $\text{cm}^{-3}$. Membrane B was additionally treated at 1400° C for 10 h. This procedure is known as post-sintering, aimed at improving the mechanical and electrical characteristics of the membranes. The samples were loaded using a four-point bending method at a constant rate (0.5 mm $\text{min}^{-1}$).

A Brüel and Kjaer (B & K) resonance transducer 8314 with main resonant frequency about 750 kHz was attached to the open end of the membrane by means of adhesive tape and silicon grease as a coupling medium. The signal obtained from the transducer was amplified by a 2638 B & K wide-band conditioning amplifier and was recordered with a *Y–t* recorder. At the same time the cumulative sum of AE counts was recorded after processing of the amplified signal with a 4429 B & K AE pulse analyser. The gain was selected so that in the absence of mechanical loading no AE signal was detected.

Fig. 1a and b illustrates the AE results during four-point mechanical loading of membranes A and B. It can be seen that the post-sintered sample, B, which has a higher fracture strength (1708 kg $\text{cm}^{-2}$) displays no AE. This may be connected with the absence of macroscopic defects in the structure as a consequence of the post-sintering

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