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Crystal Pulling and Constitution in $Pb_{1-x}Sn_xTe$

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Single crystals of $Pb_{1-x}Sn_xTe$ have been pulled from the melt using the liquid encapsulation technique and the onset of constitutional supercooling as a function of growth rate has been investigated. From the analysis of crystals and their corresponding melts, a drastically revised phase diagram of the PbTe/SnTe pseudo-binary system has been constructed.

1. Introduction

Considerable interest has recently been aroused by the discovery that PbTe and SnTe form mutual solutions in all proportions and that the energy gap, E_g, apparently varies linearly with composition, as shown in fig. 1, such that it drops to zero and then rises again with increasing SnTe concentration [1, 2, 3]. The suggested mechanism involves the exchange of conduction and valence bands at the point $E_g = 0$. Similar behaviour has also been found in the lead-rich section of the PbSe/SnSe system and better evidence for the same mechanism has, in this case, been reported [4].

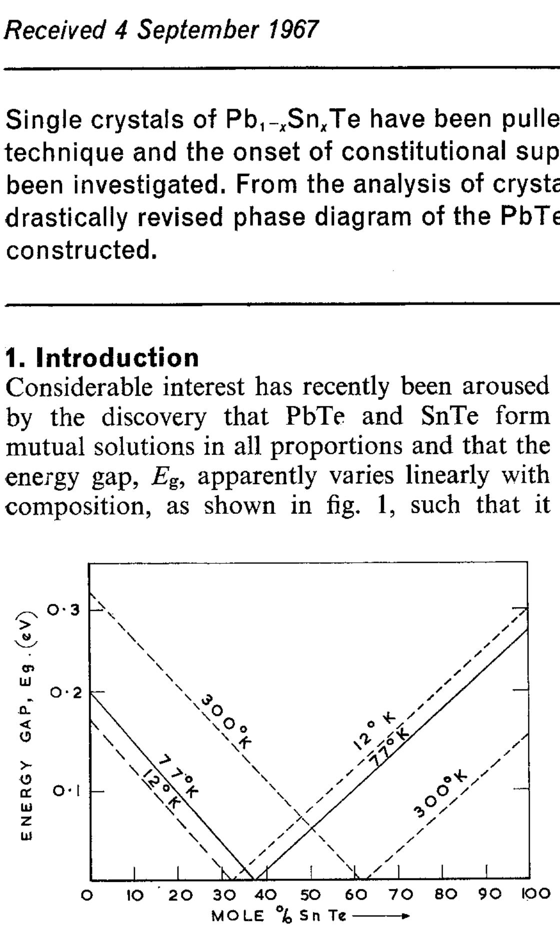

Figure 1 E_g versus composition in $Pb_{1-x}Sn_xTe$ (after [1] and [2]).

There is great interest in semiconductor lasers and detectors operating in the 10 μm region of the infrared, and lasers and photovoltaic detectors of both $Pb_{1-x}Sn_xTe$ and $Pb_{1-x}Sn_xSe$ have already been reported [1, 2, 6]. Materials have been grown by the Bridgeman technique from the melt and as crystallites and epitaxial or single-crystal layers from the vapour [7, 8]. The vertical pulling (Czochralsky growth) of these materials, however, presents two problems. Firstly, both PbTe and SnTe are appreciably volatile at their melting points and this volatility must be suppressed if the melt composition is to be maintained and visibility in the system is not to be lost; and, secondly, there is in the case of a solid solution, no congruent melting point, and the composition of a crystal must therefore differ from that of the melt from which it is pulled. This means that segregation must take place at the crystal interface as SnTe is rejected, and this condition can easily lead to constitutional supercooling resulting in an inhomogeneous cell-structure in the crystal [5].

We wish to report the vertical pulling (Czochralsky growth) of $Pb_{1-x}Sn_xTe$ single crystals from encapsulated melts [9, 10], and the revised solidus of part of the PbTe/SnTe pseudo-binary phase diagram deduced from the analysis of these crystals and their corresponding melts.

2. Experimental

The PbTe and SnTe used in these experiments were supplied by New Metals and Chemicals

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Ltd*, and were both quoted as 99.999% pure. B_2O_3, used in all cases as an encapsulant, was provided by The British Drug Houses Ltd* and was further baked-out at 1000° C in a platinum crucible under rotary pump vacuum to remove residual water and also to form the B_2O_3 into round, 25 g buttons. These buttons approximately fitted the silica crucibles above the starting materials, and, on heating, formed a sealed lid to the crucibles as soon as the softening point of B_2O_3 was reached.

To prepare alloy melts prior to growth, weighed quantities of PbTe and SnTe, totalling about 60 g, were placed in the silica crucibles and B_2O_3 caps placed above them. The crucibles, in a close-fitting graphite susceptor, were heated inductively under 1.4 to 1.8 atm of high-purity N_2 in a standard RRE† crystal puller. Bright clean melts were obtained, and there was no observable loss of material from the crucibles. It was sometimes noted, however, that there was some cloudiness in the B_2O_3 layer, and ingots analysed at this stage then showed slight losses of SnTe. This was largely due, in all probability, to the fact that the SnTe, as provided, was much more finely divided than the PbTe, and that some of the SnTe dust was therefore taken into suspension in the B_2O_3. A possible contributory cause could be that SnTe evaporates preferentially during heating, to condense as a dust on the lower side of the B_2O_3 cap, before the latter has completely melted. This dust might also be partially taken into suspension when the B_2O_3 becomes molten. It was found that the initial selection of only large, dust-free lumps of SnTe reduced these losses to negligible amounts. Ingots which had been melted-up, solidified, analysed, and then melted-up under fresh B_2O_3 showed no further loss, and the encapsulating layer remained perfectly clear.

Seeds of $Pb_{1-x}Sn_xTe$ of the required compositions were not in general available, and it was important that melt compositions should not be altered by the use of seeds of lower or zero SnTe content. Hetero-seeds of tantalum tube (1.5 mm ID, 2.4 mm OD) were therefore used. There was no evidence of attack by the melt on the seed.

Growth rates were varied between 5 cm/h and 1 mm/h in investigating the onset of cell-structure, and between 1 and 3 mm/h for good single-crystal growth. Crystals were rotated at 22 rev/min during growth. In general, crystals were "necked-in" to a diameter of 1 to 2 mm for a few millimetres after seeding-on, although this was not always necessary since the 1.5 mm "seed" formed in the tantalum-tube hetero-seed sometimes produces single crystals directly. Fig. 2 shows a necked crystal on its hetero-seed.

In most cases, especially at higher PbTe concentrations, there was a tendency for the B_2O_3 encapsulant to drain off the crystal as it emerged. In these cases, there was some loss from the top of the crystal and also growth of whiskers and crystallites, apparently on dislocations, on the crystal surface. This could probably be avoided by making additions to the B_2O_3 such as to increase its viscosity slightly.

No fully satisfactory chemical etch or polish has yet been found for $Pb_{1-x}Sn_xTe$. It was found, however, that Norr's chemical polish [11] for SnTe (dissolve 0.35 g I_2 in 40 ml C_2H_5OH and add 10 ml H_2O and 4 ml 49% HF) had a pronounced polishing effect, although it left a brown stain, and also showed cell-structure quite clearly. An example of cell-structure in a $Pb_{0.85}Sn_{0.15}Te$ crystal is shown in

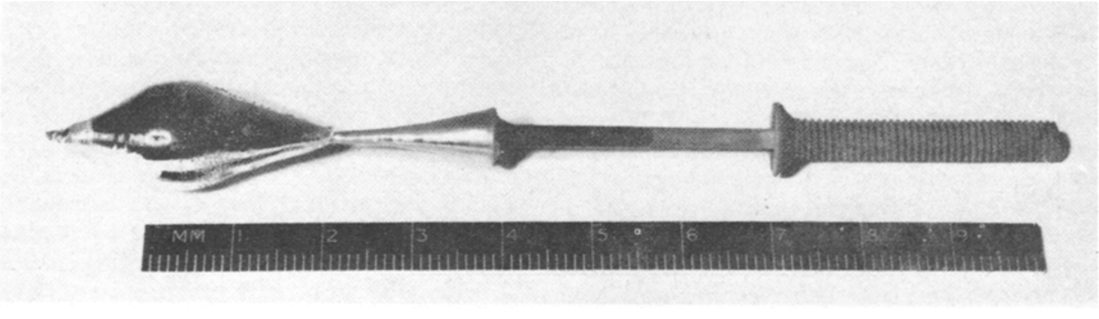

Figure 2 $Pb_{0.73}Sn_{0.27}Te$ single crystal grown at 1 mm/h through a 1 mm neck from a Ta seed.

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fig. 3. Essentially the same pattern was produced three times by repeated grinding, mechanical polishing, and re-etching, and microprobe analysis across the surface confirmed that the darker patches corresponded to Pb deficiency. It was not found possible to follow Sn concentrations by microprobe analysis owing to masking by Pb, but Te concentration could be monitored and showed no variation across the sample. Segregation is thus between PbTe and SnTe under encapsulation conditions in which stoicheiometry is maintained.

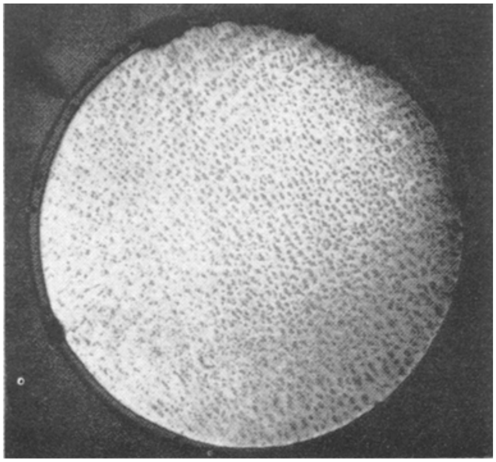

Figure 3 Cell-structure in $Pb_{0.85}Sn_{0.15}Te$ grown at 15 mm/h (×4).

Analysis of ingots and crystals was carried out by means of Debye-Scherrer X-ray patterns on powder samples removed with a fine file. Powders were annealed under vacuum at 400° C for 15 min. An experimental series of anneals at this temperature on one batch of powder for periods of up to 2 h showed no appreciable shift in composition providing anneals were kept below 1 h. 10 to 15 min were found sufficient to remove all traces of strain, and did not tend to homogenise powders from cellular materials. The relation between lattice parameter and composition in $Pb_{1-x}Sn_xTe$ has been published, and shows a small positive deviation from Vegards "law". Spot checks were carried out, and were in good agreement with both the published data [7, 12] and a recent and more complete determination [13]. Compositions determined in the present work are accurate to ±0.25 mole % although accuracies could have been increased to ±0.05% by this method, had this been necessary, since the lattice parameter varies by approximately 0.0015 Å/mole % and sharp high-angle lines were obtained.

3. Results

The present programme has divided into two parts with the production of homogeneous, single-crystal $Pb_{1-x}Sn_xTe$ of controlled composition as the ultimate aim of both. Firstly there has been the investigation of growth rate with the object of determining that rate above which constitutional supercooling sets in and inhomogeneous material results, and secondly, there has been the determination of the relevant part of the PbTe/SnTe pseudo-binary phase diagram so that the composition of crystal that will be pulled from a given melt may be accurately known.

Pull rates were varied between 1 mm/h and 50 mm/h with a constant rotation rate of 22 rev/min. The cell-structure shown in fig. 3 was produced by pulling at 15 mm/h. The composition of the crystal immediately prior to the onset of cell-structure was $Pb_{0.848}Sn_{0.152}Te$, while powder samples from the cell-structured region gave a compositional scatter of about 5 mole %. It was further established, by microprobe analysis, that segregation had in fact occurred, and was between PbTe and SnTe. Growth rates of 1 cm/h gave a suggestion of cell-structure, but nothing as dramatic as that shown in fig. 3. There is, of course, an effective annealing of the crystal during growth, which will be accentuated by the insulating layer of B_2O_3, and this process will become more effective as growth rates are reduced. It is possible, therefore, that a weak cell-structure had almost been annealed out. 5 mm/h material was apparently free of cell-structure, but, since it was not known what compositional difference is required to be shown up by the etch used, growth rates of 1 to 3 mm/h were normally used in pulling good crystals to provide a margin of safety.

The initial composition determinations on corresponding crystals and residual melts showed that the only known published phase diagram of the PbTe/SnTe pseudo-binary system [14] showed far too great a separation between the liquidus and solidus. This is very commonly found where solidi are determined by thermal analysis, and is due to extreme segregation in the solidifying ingot. It is likely, however, that the published liquidus is essentially correct, and this was then assumed to be the case in determining our revised phase diagram. So far as crystal pulling is concerned, it is the relationship between liquid and solid compositions at equal, rather than known, temperatures which is of importance since the interface temperature during crystal growth is not, in general, known.

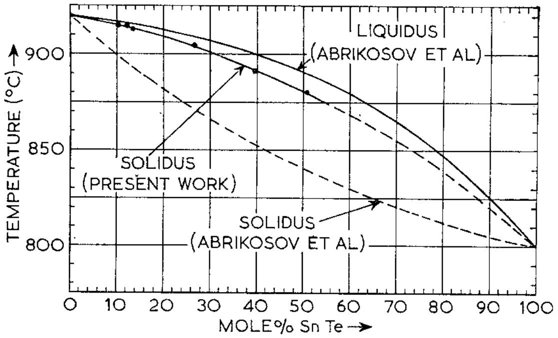

Figure 4 Phase diagram of the pseudo-binary system PbTe/SnTe. The new solidus is given with reference to the liquidus of reference 14, and the old solidus is shown as a fully broken line for comparison.

To determine the tie-lines in the phase diagram, powder samples were taken of the first and last materials to crystallise, and from various parts of the residual melts, and these were analysed as described above. Compositions from different parts of the same melt were found to agree well. The melt compositions were found on the assumed liquidus, and the corresponding crystal compositions plotted at the same temperatures. When compositions of the first material to crystallise were taken to correspond to initial melt compositions calculated from the weighed components, a considerable scatter of solidus points was observed, and the compositional shift of melts on being made up was thus detected. Thereafter, melts for this purpose were made up, and very small crystals (~1 g) were pulled and then both the melt and the entire small crystal were analysed before the pulling of a large crystal.

The revised PbTe/SnTe pseudo-binary phase diagram is shown in fig. 4. The solidus determined in the present work is given relative to Abrikosov's liquidus, and Abrikosov's solidus is shown for comparison.

4. Conclusions

It has been established that single crystals of $Pb_{1-x}Sn_xTe$ can be pulled from the melt to closely controlled compositions, using the liquid encapsulation technique. Evidence of cell-structure in the crystals, due to constitutional supercooling and segregation at the growing interface, has been found for pull rates of 10 mm/h and more, and it has been proved that segregation is between PbTe and SnTe such that the Te concentration remains constant. It is possible, however, that constitutional supercooling sets in at lower pull rates, but that the cell-structure thus formed is largely annealed out when the crystal is kept close to its melting point for longer periods of time.

Analysis has been made of the first and last materials to crystallise and of their corresponding melts by X-ray diffraction and, from these results, a revised PbTe/SnTe pseudo-binary phase diagram, markedly different from the only version previously published, has been constructed and presented. This will allow the growth of $Pb_{1-x}Sn_xTe$ crystals of controlled composition by any melt growth technique.

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