JOURNAL OF MATERIALS SCIENCE 4 (1969) 313–319

Micro-Indentation Hardness Variation as a Function of Composition for Polycrystalline Solutions in the Systems PbS/PbTe, PbSe/PbTe, and PbS/PbSe

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Received 16 August 1968

Vickers micro-indentation hardness as a function of composition has been measured for polycrystalline solutions of lead chalcogenide systems and results compared to exsolution tendencies as implied by subsolidus features of the phase diagrams. Each system exhibited a positive deviation from a linear hardness relation between the end member compounds. The most pronounced hardening was observed for PbS/PbTe solutions; the maximum hardness occurs at about 30 mole % PbTe, coincident with a large solubility gap with a solvus maximum (critical point) at about 30 mol % PbTe and approximately 805° C. The least amount of hardening was observed for the system PbS/PbSe, which exhibits no exsolution at temperatures as low as 300° C. The hardness versus composition curve was approximately symmetric about the 50 mol % composition. Intermediate between these two systems, the PbSe/PbTe crystalline solutions exhibited an asymmetric hardness/composition curve with maximum hardness at about 30 mol % PbTe. Partial phase studies indicate the possibility of a solvus maximum at 500 to 600° C on the PbSe-rich side of the diagram.

1. Introduction

Two effects are responsible for hardening in two-component metallic systems: solid solution-hardening if the components form a continuous solution, and precipitation-hardening if the two components exsolve into separate compounds. Few data are available for non-metallic systems but there seems to be no reason to suspect that similar principles would not hold.

In this paper we raise the question of the hardness response to the intermediate case in which solid solution is complete but where there is a tendency toward exsolution. As an example of a set of binary systems in which exsolution becomes progressively more probable, we have selected PbS/PbSe, PbSe/PbTe, and PbS/PbTe. Exsolution is well established in PbS/PbTe, is probable in PbSe/PbTe, and unlikely in PbS/PbSe. Continuous solid solutions prepared at temperatures above the solvus are homogeneous in the phase rule sense but must contain an increasing number of clusters and compositional inhomogeneities close to the critical radius and probably below the detection limit by X-ray and related methods as the temperature of the solvus is approached. We investigate the response of the microhardness to these fluctuations and therefore of its use as a characterisation tool for the detection of incipient phase separation.

1.1. Phase Equilibria in the Lead Chalcogenides

A summary of the available information on phase equilibria of the lead chalcogenides is given in fig. 1. The PbS/PbTe system is reproduced from an earlier paper [1]. The solidus and

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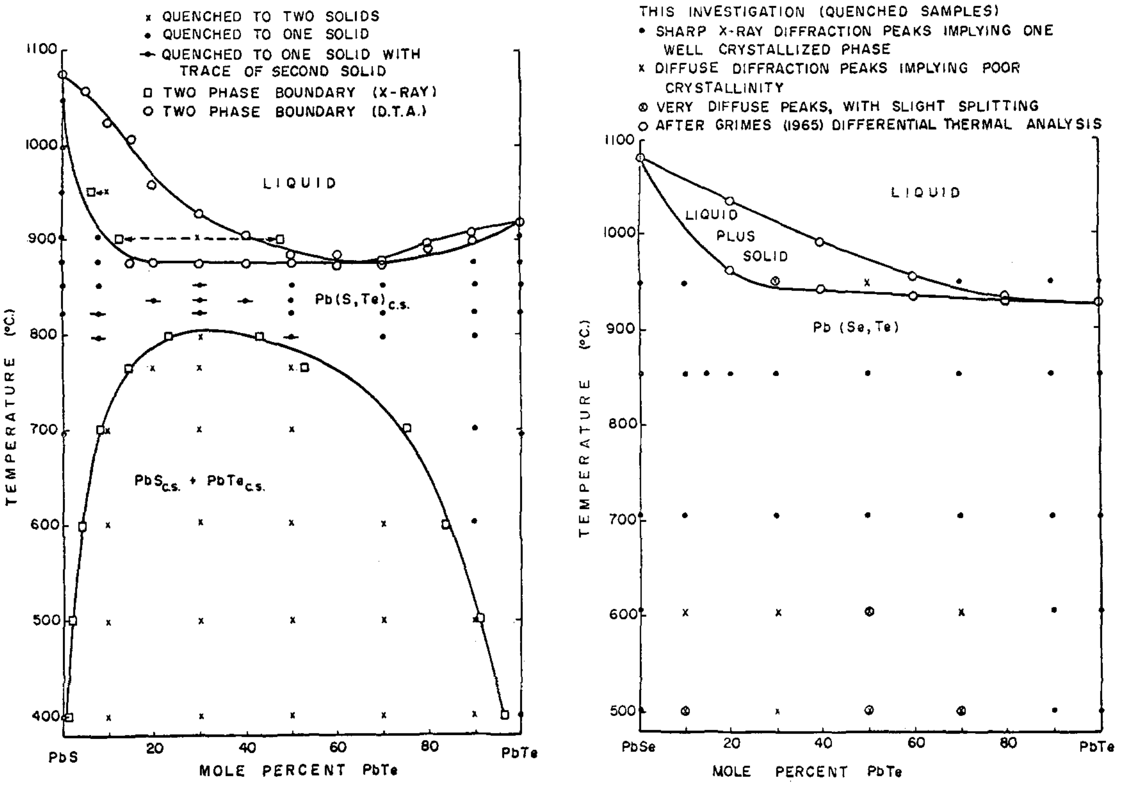

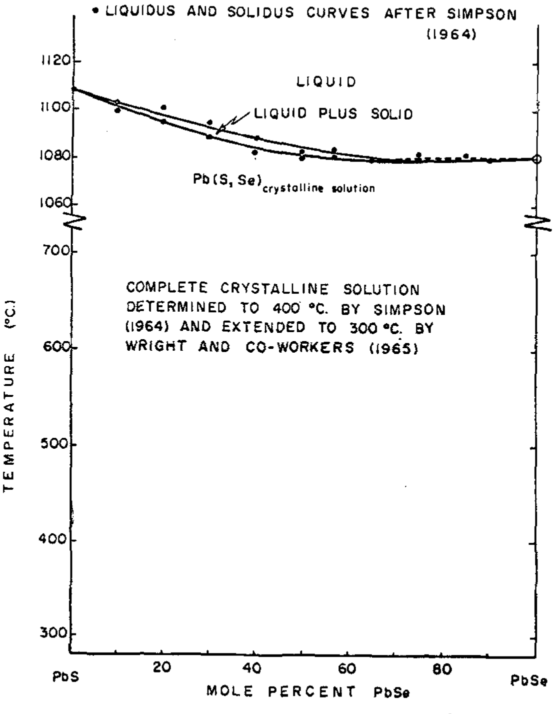

Figure 1 Phase diagrams for the systems PbS/PbTe [1], PbSe/PbTe ([2] and this investigation), and PbS/PbSe [3, 4].

liquidus of the system PbSe/PbTe were taken from Grimes [2]. Many additional experiments were performed in the sub-solidus region to search for possible exsolution. The diagram for the PbS/PbSe system was constructed from various literature sources [3, 4].

The PbS/PbTe system exhibits a pronounced minimum in the liquidus and a solvus with a critical point at 805° C at a composition of 30 mol % PbTe. The PbSe/PbTe system has a distorted liquidus curve, implying some non-ideality of the solid solution, but the solvus, if one exists, has not been observed experimentally. Experiments at temperatures below 600° C produced materials with diffuse X-ray reflections and some peak splitting. These results could be due to sluggish kinetics or they could hint at the existence of a solvus below 600° C, probably skewed to the PbSe-rich side. The system PbS/PbSe exhibits a more uniform liquidus and there is no evidence for phase separation at temperatures as low as 300° C.

1.2. Previous Hardness Data for the Lead Chalcogenides

General reviews of microhardness techniques have been published by Mott [5], Bückle [6], and Young and Millman [7].

A number of authors [7-10] have reported microhardness measurements made on PbS, but the data for PbSe and PbTe are limited. These results cannot be readily compared to the data of this investigation because most references do not include complete experimental data.

The large range of values reported by Bloem and Kröger [8] were a result of studies of hardness as a function of sulphur pressure during sample preparation, thus reflecting stoichiometric effects. Seltzer's [9] studies also include variation with carrier concentration as well as annealing temperature and loads.

A literature survey has revealed only one paper reporting any data on microhardness of lead chalcogenide crystalline solutions. This work by Sindeyeva and Godovikov [10] includes a very limited number of measurements, made during their phase studies on the PbS/PbTe and PbS/PbSe systems, mostly on partially exsolved samples.

2. Experimental

2.1. Synthesis of Materials

Starting materials consisted of powders of the end member compounds. PbS and PbTe were purchased commercially, and a semi-quantitative spectrochemical analysis of cation impurity has been given elsewhere [1]. PbSe was synthesised from the elements and an analysis of the compound showed the cation impurity to be less than 0.01 %. The main impurities were Fe, Si, Bi, and Sn.

The powders were weighed to the desired mole ratio, and mechanically mixed in plastic vials in a mixer mill. The mixtures were then sealed in evacuated silica tubes, heated in a vertical resistance furnace, and finally quenched by dropping the capsules into cold water. Temperatures for most runs were controlled to ± 5° C or better, and measured with chromel-alumel thermocouples. Specific thermal histories for all samples are given in table I.

Powder patterns of the reacted samples were taken on a Norelco diffractometer to determine the number of phases present. Lattice parameters were measured at $\frac{1}{4}°$ (2θ) per minute using an external silicon standard. The homogeneity of selected samples was also studied with an electron probe and/or electron microscope. For the latter, fresh fracture surfaces were replicated with a carbon platinum film.

To obtain coarse-grain, well-crystallised materials of PbS/PbSe solutions, the mechanical mixtures were first held above the liquidus temperature for 1.5 h. A graphite liner was used to separate the melt from the silica walls. The furnace temperature was then reduced, and the

TABLE I Results of Vickers micro-indentation hardness (HV) measurements for lead chalcogenide crystalline solutions. HV (kg/mm^2) represents average of ten measurements per sample.

PbS/PbTe				PbSe/PbTe		PbS/PbSe		
Comp. (mole % PbTe)	HV 15 g load	HV 40 g load	Annealing T° C (time-hours)	Comp. (mole % PbTe)	HV 15 g load	Comp. (mole % PbSe)	HV 15 g load	Annealing T° C (time-hours)
100	43.8	37.8	852 (23)	100	40.4	100	57.0	1004 (24)
100*	55.6	*	852 (24)	90	48.8	90	73.8	1004 (24)
95*	73.2	*	852 (24)	70	68.5	70	87.6	1004 (24)
90	82.4	69.1	851 (25)	50	82.8	50	92.5	1003 (24)
75*	121.2	*	852 (24)	30	98.4	40	101.0	1007 (24)
70	126.5	97.0	851 (25)	20	87.9	30	89.7	1007 (24)
65*	141.9	*	852 (24)	15	90.7	20	83.3	1007 (24)
50	147.6	127.8	851 (25)	10	83.1	10	83.9	1003 (24)
40	156.1	122.9	838 (27)	0	58.3	0	73.1	1003 (24)
30	148.9	128.7	851 (25)					
20	155.6	112.5	838 (27)					
10	138.6	112.3	851 (25)					
0	93.7	74.6	852 (23)					

Additional Thermal History of Samples

System PbS/PbTe: mixed powders of end member compounds reacted in one crystalline phase region and quenched after time indicated.

*Melted prior to annealing (hardness not measured for 40 g load).

System PbSe/PbTe: mixed powders of end member compounds reacted at 853° C for 24 h and quenched.

System PbS/PbSe: mixed powders of end member compounds melted prior to annealing and quenching.

samples allowed to anneal below the solidus temperature, at approximately 1000° C, for 24 h before quenching. Subsequent powder diffraction analysis showed well crystallised, one-phase material for all samples, and lattice parameter measurements were in good agreement with previously reported results [11]. In addition, electron micrographs did not exhibit any evidence of micro-segregations.

In the system PbS/PbTe, samples of 65, 75, 95, and 100 mol % PbTe were also prepared by initially melting the powders before annealing for 24 h between the solvus and solidus temperatures at approximately 850° C. Although powder diffraction and electron probe analysis indicated these materials to be single-phase, electron microscopy studies showed what appeared to be segregations in the crystalline solutions. In general, however, attempts to melt PbS-rich compositions resulted in explosions or implosions of the silica tubes, even when a graphite crucible was used to separate the material from the silica. Because of this, it was necessary to use samples reacted and sintered for 24 h in the solid state at the same temperature. These samples were not as well crystallised, but X-ray diffraction indicated that all were single-phase except compositions quenched from near the top of the solvus (20, 30, and 40 mol % PbTe) whose diffraction patterns showed some slight peak-splitting. A discussion, including lattice parameter measurements for samples reacted in the solid state, has been published elsewhere [1]. Electron microprobe analysis for sample homogeneity was inconclusive.

Finally, samples in the system PbSe/PbTe were reacted below the solidus, at 853° C for 24 h. Results to be presented for the system PbS/PbTe, show that the general trend of hardening for samples reacted in the solid state is the same as for those melted prior to annealing. For this reason, and because of the problem of explosions, samples in the PbSe/PbTe system were not initially melted. All samples in this system were analysed by powder diffraction, as well as electron probe scans, and no inhomogeneities were detected.

2.2. Specimen Preparation

For the hardness measurements it was necessary that all samples had a polished surface that could be positioned perpendicular to the vertical indenter. This was readily accomplished by surrounding the sample with a self-curing resin in a plastic ring about $\frac{1}{2}$ in. (12.5 mm) diameter by $\frac{1}{4}$ in. (6.25 mm) deep. When the resin had hardened, the disc was removed from the ring, and one surface ground with 600 mesh grit until a sufficient area (about 3 mm square) of the sample was exposed, and finally polished with diamond paste. Indentations on specimens prepared by melting and annealing could be made without spanning any scratches visible at the magnification of the indenter microscope (400 ×). This required scratch-free areas of 12 to 45 μm, depending on sample composition and load, for each indentation. Polishing of the samples reacted in the solid state was not as effective. The reverse side of the disc was ground parallel to the polished surface so that it could be aligned parallel to the indenter stage orthogonal to the indenter. All samples were thoroughly rinsed with water and given a final cleaning with ether immediately preceding the measurements.

2.3. Hardness Measurements

Microhardness measurements were made with a Leitz Miniload Hardness Tester and reflecting microscope. A Vickers pyramidal diamond was used to make the indentations, and a micrometer eyepiece on the microscope allowed the diagonals of the resulting diamond-shaped indentations to be measured with an estimated accuracy of ± 0.5 μm. Ten indentations were made and measured for each sample. After the first five measurements, the sample was repositioned, and the remaining five indentations made in a new area. After the indenter had completed its descent, it was allowed to remain on the sample for 8 sec before being raised. It was found however, that load times up to at least 30 sec did not produce any appreciable creep or flow. Testing with different loads showed that up to 100 g could be used without causing microcracks to emanate from the indentations. Because of the small particle sizes of most samples reacted in the solid state, however, the 15 g load was determined to be the optimum weight producing consistently good indentations for most samples. Thus all three systems, for comparison, were measured with this load.

3. Experimental Results

The Vickers microhardness values measured for the three lead chalcogenide systems are listed in table I.The variation of hardness as a function of composition is plotted in figs. 2 to 4. Both the arithmetic average and the range of ten measure-

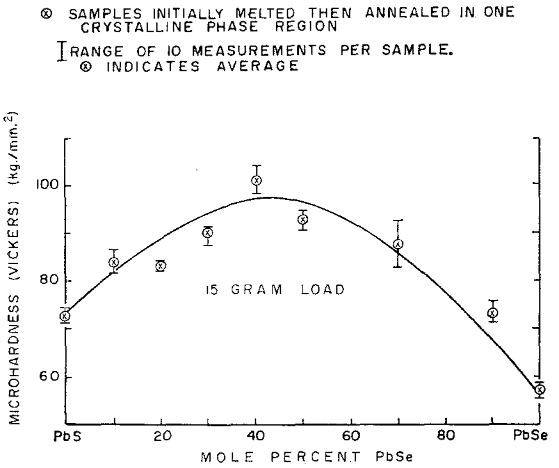

Figure 2 Microhardness (Vickers) versus composition plot for the system PbS/PbSe (15 g load).

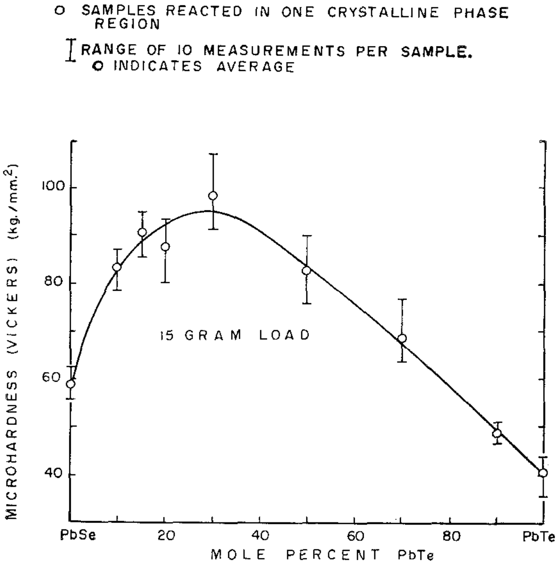

Figure 3 Microhardness (Vickers) versus composition plot for the system PbSe/PbTe (15 g load).

ments for each sample is shown. For comparison, all figures are plotted on the same scale. An additional set of measurements, using a 40 g load, was made on the PbS/PbTe system and the results are included in table I and plotted in fig. 5.

In each system a positive deviation from a linear hardness relation between the end members was observed. In the system PbS/PbSe, the hardness composition curve appears relatively symmetric, with Vickers values (kg/mm^2) rising

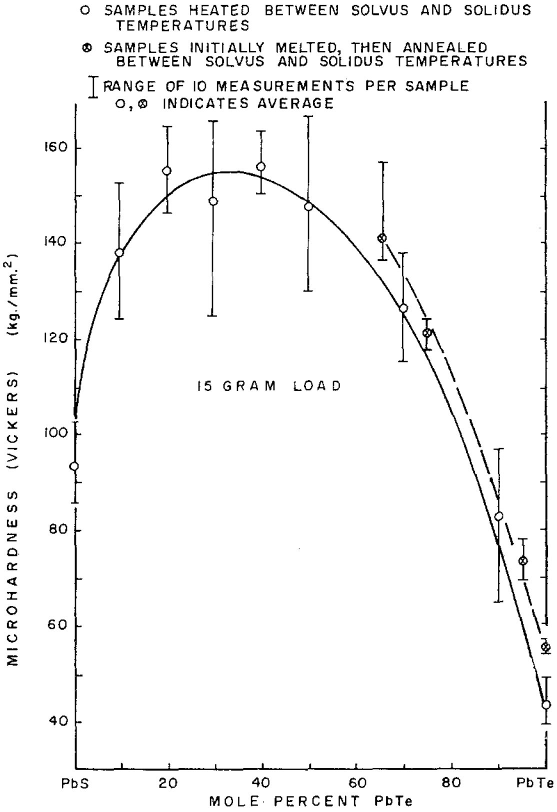

Figure 4 Microhardness (Vickers) versus composition plot for the system PbS/PbTe (15 g load).

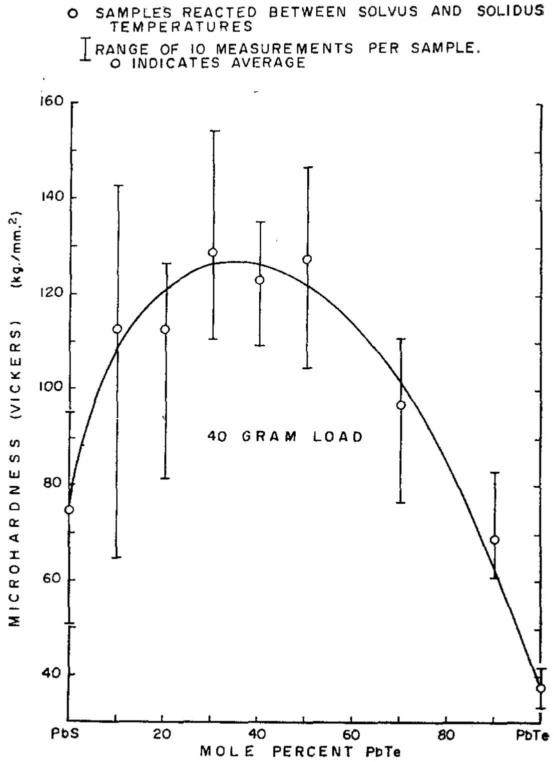

Figure 5 Microhardness (Vickers) versus composition plot for the system PbS/PbTe (40 g load).

from 73 for PbS to a maximum of about 100, then falling to 57 for PbSe. The hardness of the $PbSe_xTe_{1-x}$ series reaches a peak near 100 kg/mm, but the curve is asymmetric with the maximum occurring at about 30 mol % PbTe. Vickers values for the end members, which had the same thermal history as the crystalline solutions, are 58 for PbSe and 40 for PbTe.

The maximum hardness in the system PbS/PbTe is considerably higher, reaching 150 to 160 kg/mm^2, at about 30 mol % PbTe. Although the range of values for each sample is much larger than in the other systems, the trend of hardening as a function of composition is still evident. In addition, the Vickers values for the samples of 20, 30 and 40 mol % PbTe, whose diffraction patterns showed some evidence of separation, still seem to fit the general hardening pattern. The hardness versus composition curve (fig. 4) also shows the results of measurements made on the four samples melted prior to annealing. Although this type of preparation appears to increase the Vickers values, the general shape of the curve is similar to that for the samples reacted in the solid state. Both sets of samples were quenched after annealing at approximately the same temperatures for similar periods of time (table I). Results using the 40 g load (fig. 5) show the same trend in hardening, but reflect a decrease in the Vickers values with increased load. This is an expected phenomenon and is discussed by Bückle [6].

To provide a clearer basis of comparison, results of the measurements for all three systems have been replotted in fig. 6 to show the per cent deviation of Vickers hardness from linearity as a function of composition. Although the scatter is fairly large within each system, the deviation from a linear hardness relation is clear for each set of crystalline solutions, with Pb (S, Te) showing the largest and Pb (S, Se) the smallest relative in change in hardening. It is also interesting to note that this method of representation appears to reduce the discrepancies of Vickers values for the two different loads used for the system PbS/PbTe.

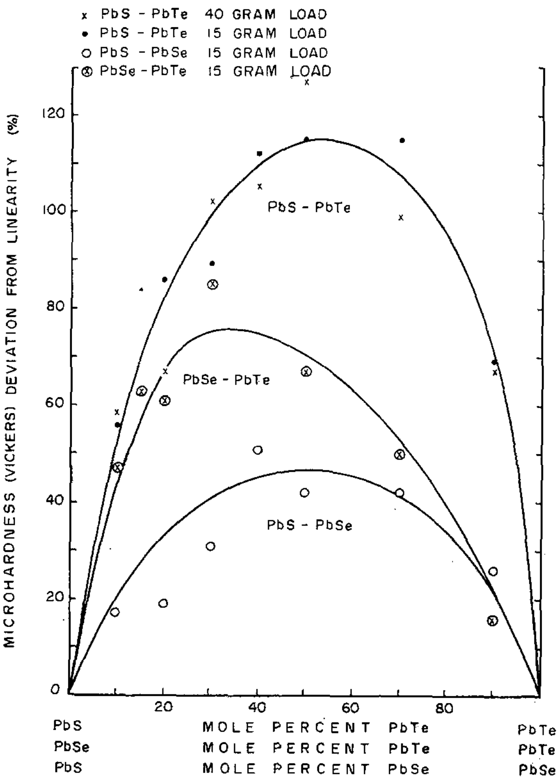

Figure 6 Microhardness (Vickers) per cent deviation from linearity plot as a function of composition for the systems PbS/PbTe, PbSe/PbTe, and PbS/PbSe.

4. Discussion

Microhardness studies of non-metallic solid solutions are uncommon in the literature, and often the investigations are sketchy, in some cases covering only a limited range of the crystalline solution, and in others, the emphasis is directed to intentionally exsolved material and includes no comparison to homogeneous samples. In most instances, where the complete range of solution has been studied and reported, a positive deviation from linearity has been observed with maximum hardness occurring at about 50 mol %. Examples of this type are the systems KCl/KBr, CaF_2/SrF_2, SrF_2/BaF_2, NiO/CoO [12] and GaSb/AlSb [13]. The system SnTe/PbTe [14] has been reported as showing an almost linear relation between the end members, and at least one system $(Fe,Mn)WO_4$ [7], shows both a maximum and minimum in hardness as a function of the cation ratio.

To the authors' knowledge, sub-solidus relations in most of these systems have not been studied in detail at temperatures much below the solidus, and it is not possible to make any general observations regarding hardness versus exsolution tendencies as exhibited by the phase diagrams. Results of the measurements on the lead chalcogenide systems, however, offer a clearer opportunity to observe the possibility of such a correlation.

The largest deviation occurs in the system PbS/PbTe whose phase diagram exhibits a well-defined solvus. Although X-ray diffraction and electron microscopy studies show some phase separation taking place, the continuity of the hardness versus composition curve suggests that the increased hardening in this system is not due to simple precipitation hardening alone. The intermediate case is PbSe/PbTe where phase equilibria data indicate a tendency to segregation in the solid state although the solvus, if it exists, is below the kinetic threshold of measurement by the technique used. Finally, the system PbS/PbSe, in which the phase diagram shows little evidence for any tendency for exsolution, also exhibits the minimum hardening.

The tentative conclusion reached from this study is that microhardness measurements are sensitive to the clusters and compositional inhomogeneities which must exist in solid solution systems with a solvus. This "cluster hardening" is intermediate in magnitude between solid solution-hardening and precipitation-hardening. Application of hardness measurements as a characterisation tool for clustering and incipient phase separation in solid solutions is limited, however, by the necessity of first accounting in some way for intrinsic solid solution-hardening effects.

Acknowledgement

We are grateful to J. B. Halbig for the synthesis of the PbSe, and to R. Bradt for commenting on the manuscript. This work was supported by the Advanced Research Projects Agency of the Department of Defense under contract DA-49-083 OSA 3140.

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