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STUDY OF THE SILVER SELENIDE–SILVER TELLURIDE SYSTEM

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ABSTRACT

The system Ag_2Te–Ag_2Se was investigated by DTA, X-ray diffraction and microstructural analysis within the composition interval from 0 to 100% Ag_2Te. Samples obtained after heating at 500°C for 720 h were studied.

The high-temperature polymorphs form a continuous solid solution with a minimum at 35% Ag_2Te and 835°C. At low temperatures solid-phase transformations take place. The break-down of the solid solution proceeds eutectoidally at about 110°C on the Ag_2Te side and peritectoidally at about 150°C on the Ag_2Se side. The system Ag_2Te–Ag_2Se is rather complex.

INTRODUCTION

The system Ag_2Se–Ag_2Te is a quasi-binary join of the ternary system Ag–Se–Te along the straight line Ag_2Se–Ag_2Te.

Ag_2Se is the only compound in the system Ag–Se. It has a melting point[1] of 898°C.

Ag_2Te is one of the silver–tellurium compounds. On the phase diagram it is characterized by a distectic point[1] at 960°C.

The two compounds have a narrow energy gap and are promising thermoelectric materials with $Z = 2.1 \cdot 10^{-3}$–$3.0 \cdot 10^{-3}\,°C^{-1}$ between 100 and −180°C[2–4] for Ag_2Se and $Z = 1.3 \cdot 10^{-3}\,°C^{-1}$ for Ag_2Te, also determined at low temperatures[5].

According to Joffe[6] the complication of the composition of the semiconductor materials leads to the improvement of some of their properties, particularly of the thermoelectrical ones. This is why the study of the phase diagram of the system Ag_2Se–Ag_2Te is of interest in order to find a solid solution region which could bring about a smooth change in the properties of the materials obtained.

In the literature there are no data concerning the phase diagram of the system. Studies have been carried out on some electrophysical properties of pressed samples in the system[7] and on the influence of various etching agents in order to select the most appropriate one both for cast and annealed samples[8].

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TABLE 1

PHASE TRANSITION TEMPERATURES OF Ag_2Se AND Ag_2Te

Compound	*Transition temp. (°C)*	*Symmetry*	*Cell dimensions (Å)*	*Ref.*
Silver selenide	133	cubic	$a = 4.983$	11
	425		—	13
	133	orthorhombic	$a = 4.333$ $b = 7.062$ $c = 7.764$	15
	128–133	orthorhombic	$a = 7.06$ $b = 4.34$ $c = 7.80$	16
Silver telluride	145	monoclinic	—	10
	802.3	cubic f.c.c.	—	10
	145	monoclinic	$a = 6.57$ $b = 6.14$ $c = 6.10$ $\beta = 61.15°$	12
	145	monoclinic	$a = 8.09$ $b = 4.48$ $c = 8.96$ $\beta = 123.20°$	14

In the system Ag_2Se–Ag_2Te one could expect the existence of a solid solution based on anionic substitution. The size factor, determined by Hume–Rothery's rule[9], is favourable for both anions, the type of the chemical bond is also similar: at high temperatures it is metallic and covalent–ionic at low temperatures.

The two compounds exist as several polymorphs. Upon polymorphic transition the symmetry changes from low to cubic.

The temperatures of the phase transitions of the two compounds are given in Table 1.

In the literature[17–21] there are also other data but these have been either obtained on thin films with a stoichiometry open to discussion or have remained unconfirmed by other authors. Therefore, we shall refrain from considering them in the present paper.

The difference in the polymorphic transition temperature is also considerable: for Ag_2Se from 122°C[22] to 166°C[18] and for Ag_2Te from 140°C[10] to 157°C[20].

EXPERIMENTAL

Silver selenide was obtained from silver of purity 99.999% and selenium of purity 99.999% in stoichiometric amounts by isothermic direct synthesis at 1000°C in a quartz vessel at a residual pressure of 10^{-3} Torr and subsequent annealing from 900°C in a mixture of water and ice.

Silver telluride was obtained in the same way starting from silver of purity 99.999% and tellurium of purity 99.9995%.

Samples of silver selenide and telluride synthesized in this way were sintered within the entire concentration range from 0 to 100% Ag_2Te, at 5 mol% intervals.

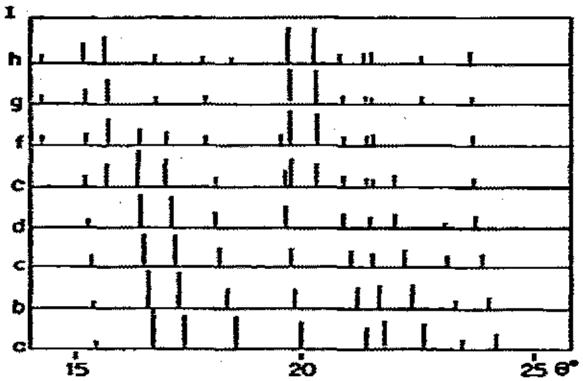
The samples were treated at 500°C for 720 h. This temperature was selected on the basis of DTA patterns of untreated samples.

After annealing the samples were quenched. It should be noted that the silver-rich samples proved unamenable to quenching. This is also characteristic for the system[23] Ag_2Se–PbSe.

TABLE 2

THERMAL EFFECTS IN THE SYSTEM Ag_2Se–Ag_2Te

Composition (*mole %*) *Ag_2Te*	*Temperature (°C)* *Heating*				*Cooling*	
0		135			900	
5		140			870	898
10	110				870	890
15		140			880	
20	110	145			855	880
25	110				840	875
30	110	140			840	865
35		143			835	
40	118	140				852
45		140			840	860
50		140			855	
55		140			850	890
60	110	140		490	858	
65		142			860	880
70		140			870	910
75	118				880	905
80	110	140		665	890	930
85	110			690	890	940
90		135	485	710	930	
95		140	690	740	940	
100		148		737	955	



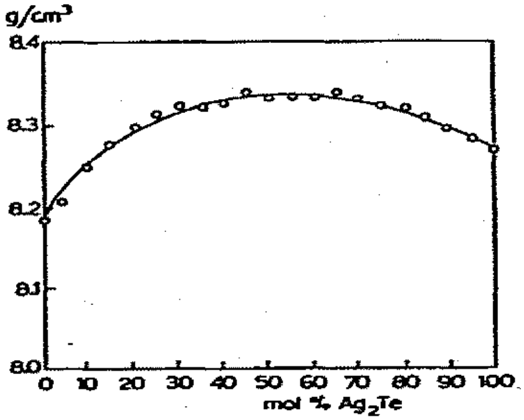


Fig. 1. X-ray powder patterns of the system. a = 100% Ag_2Se; b = 20% Ag_2Te; c = 35% Ag_2Te; d = 45% Ag_2Te; e = 60% Ag_2Te; f = 85% Ag_2Te; g = 92% Ag_2Te; h = 100% Ag_2Te.

Fig. 2. Microhardness in the system Ag_2Se–Ag_2Te.

This may be explained by the difference in the structure of α-Ag_2Se (b.c.c. lattice) and β-Ag_2Se (orthorhombic). Some data point to the fact that the b.c.c. lattice is usually stable at high temperatures while at low ones it transforms easily into a tetragonal and an orthorhombic lattice[24].

DTA was performed on a Paulik, Paulik–Erdey instrument at a heating rate of 10°C min^{-1} and a standard substance Al_2O_3. The samples were introduced in quartz vessels evacuated to a pressure of 10^{-3} Torr. In this way only heating effects were recorded. The cooling curves were obtained by means of an experimental set-up devised by us.

The thermal effects obtained from 21 samples in the system Ag_2Se–Ag_2Te are given in Table 2.

The X-ray powder diffraction examinations were performed on ground and annealed samples. The results are summarized in the bar diagram illustrated in Fig. 1 and refer to samples annealed at 350°C. The existence of a solid solution region up to 50 mol % silver telluride can be seen.

Diffraction lines are shifted to smaller Bragg angles, which indicates an increase in the cell dimension. This is easily explained by the larger ionic radius of Te^{2-}. An opposite dependence is observed on the silver telluride side, up to 8 mol% silver selenide.

The microstructure was studied by etching well-polished sections with a mixture of NHO_3:CH_3COOH:H_2O (2:2:3) at 70–95°C (etching time 5–10 sec).

The microstructure (Fig. 2) revealed the existence of both one- and two-phase samples. The grain size in the one-phase samples is about 0.25 mm.

The microhardness was measured on the etched surface. 30 measurements were performed for each phase. The results were then treated by a generally adopted method.

The measurement of the microhardness yielded for the pure components results which are in comparatively good accord with the literature data[25]. The introduction of a third component brings about a considerable change in micro-

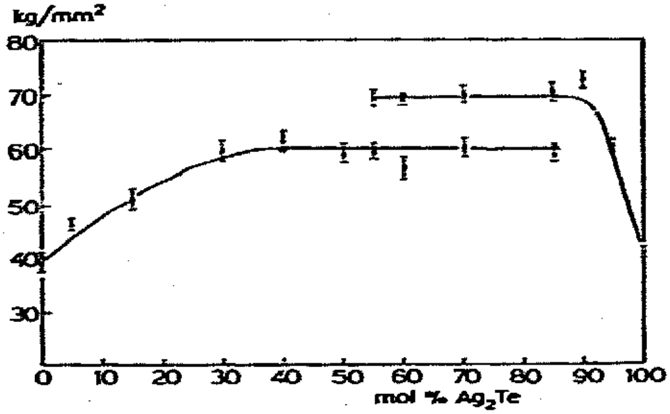


Fig. 3. Density in the system Ag_2Se–Ag_2Te.

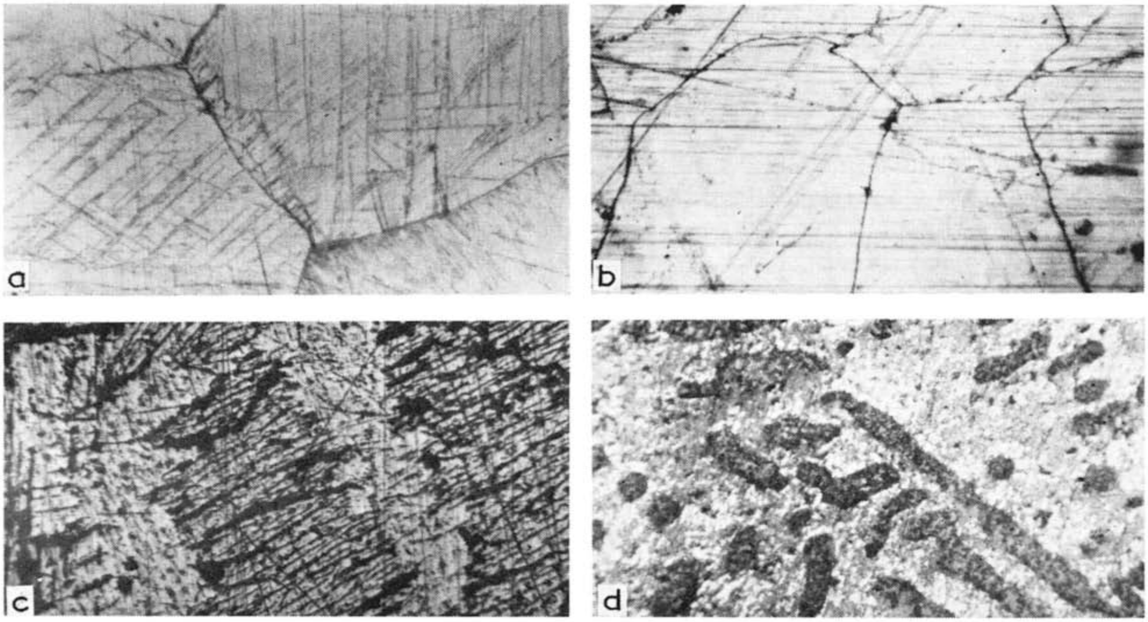


Fig. 4. Microstructures in the system Ag_2Se–Ag_2Te. a = 10% mol Ag_2Te; b = 10% mol Ag_2Te; c = 55% mol Ag_2Te; d = 70% mol Ag_2Te.

hardness (Fig. 3). This is probably due to a change in the crystal lattice brought about by the solid solution. The two-phase region displays a microhardness corresponding to that of the limiting solid solutions.

The density of the samples was determined hydrostatically. It varied from 8.18 to 8.27 g cm^{-3} (Fig. 4).

RESULTS

The Ag_2Se–Ag_2Te system was studied by DTA, X-ray powder diffraction and microstructural analysis.

The high-temperature polymorphs α-Ag_2Se and α'-Ag_2Te form a continuous solid solution with a minimum at 35 mol% Ag_2Te and at 835°C (Fig. 5). Below the solidus line complex transformations take place. They are brought about by the polymorphism of silver selenide and silver telluride. The latter undergoes a transformation α'-$Ag_2Te \rightleftarrows \alpha$-$Ag_2Te$ at about 800°C and this narrows the solid solution region based on the high-temperature modifications of Ag_2Te and Ag_2Se.

At 600°C the solid solution region extends from α-Ag_2Se to 75 mol% α-Ag_2Te.

Further decrease in temperature leads to the narrowing of the solid solution region: at 350°C Ag_2Se dissolves about 50 mol% Ag_2Te and Ag_2Te dissolves about 10 mol% Ag_2Se.

At 100–150°C Ag_2Se, Ag_2Te and the solid solutions based on them undergo new polymorphic transitions

α-$Ag_2Se \rightleftarrows \beta$-$Ag_2Se$ α-$Ag_2Te \rightleftarrows \beta$-$Ag_2Te$

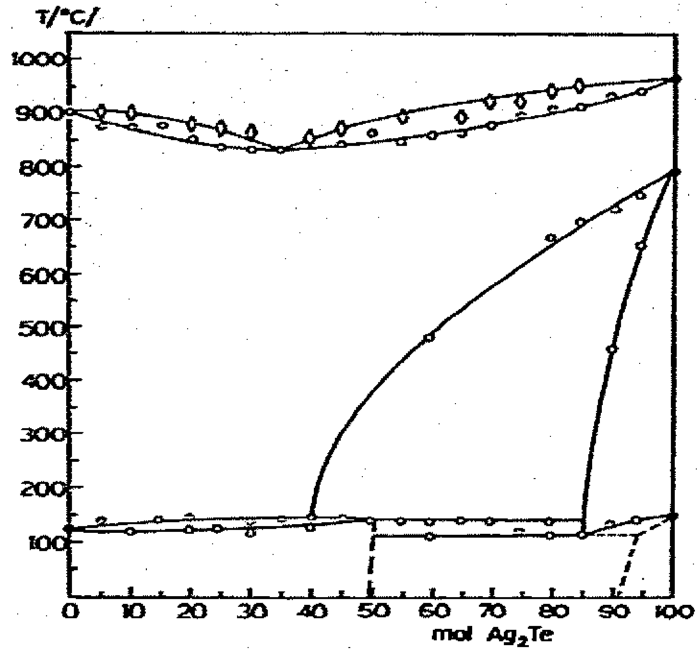


Fig. 5. Phase diagram in the system Ag_2Se–Ag_2Te. ○, Effects obtained upon heating; ◊, effects obtained upon cooling.

The transitions in this region are given only tentatively since a very long annealing time is required for equilibrium to be reached at such low temperatures (equilibrium was not reached at 100°C after a 1000-h annealing: a mixture of the two modifications is observed).

The breakdown of the solid solutions takes place eutectoidally on the Ag_2Te side and peritectoidally on the Ag_2Se side. The temperature of the eutectoid transition is about 110°C and of the peritectoid one at about 150°C for compositions of 80–85 mol% Ag_2Te and 40 mol% Ag_2Te, respectively.

Below the temperature of the peritectoid transformation a solid solution region based on the low-temperature polymorphs of the two components exists: up to 50 mol% Ag_2Te on the Ag_2Se side and up to 8 mol% Ag_2Se on the Ag_2Te side.

The diagram shows that with the addition of Ag_2Te the temperature of the $\beta \rightleftharpoons \alpha$ transition increases. The opposite phenomenon is observed for Ag_2Te.

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