Bull. Mater. Sci., Vol. 15, No. 4, August 1992, pp. 367–375. © Printed in India.

Low-temperature synthesis and characterization of $Ag_2S_{1-x}Te_x (0 \leqslant x \leqslant 1)$

H N VASAN and A K SHUKLA
Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India

MS received 15 January 1992

Abstract. A low-temperature route for the synthesis of Ag_2S, Ag_2Te and their solid solutions $Ag_2S_{1-x}Te_x$ $(0 \leqslant x \leqslant 1)$ is reported. Ag_2S is prepared by the direct addition of silver nitrate solution to thiourea, while Ag_2Te is prepared by reacting silver nitrate solution with tellurium in nitric acid and subsequently reducing it with hydrazine hydrate. The solid solutions of Ag_2S and Ag_2Te are obtained by the addition of nitrate solutions of silver and tellurium to thiourea followed by its reduction with hydrazine hydrate. The method enables the synthesis of low-temperature crystalline phase of $Ag_2S_{1-x}Te_x$ solid solutions. The powder X-ray diffraction studies suggest that the solid solutions of compositions $x < 0{\cdot}3$ have a phase akin to α-Ag_2S and those with compositions $x > 0{\cdot}6$ are similar to α-Ag_2Te. In the intermediate range of compositions ($x = 0{\cdot}4$ and $0{\cdot}5$), the solid solutions are found to be mixtures of α-Ag_2S and α-Ag_2Te phases which transform totally to α-Ag_2S phase on prolonged annealing at about 473 K.

Keywords. Low-temperature synthesis; silver chalcogenide; Ag_2X characterization.

1. Introduction

Silver chalcogenides, Ag_2X(X = S, Se, Te) being mixed conductors are potential materials for certain applications such as solid-state coulometers and battery electrodes. These materials undergo a structural α to β phase transition at about 423 K accompanied by a marked increase in their electronic and ionic conductivities (Wagner 1953; Miyatani 1958, 1959, 1960; Shukla and Schmalzried 1979; Shukla *et al* 1981; Sohege and Funke 1984, 1989). One could synthesize these chalcogenides by the solid-state reaction of the constituent elements. But a similar method for preparing the solid solutions of Ag_2S and Ag_2Te results either in the formation of an amorphous phase or the high temperature β-phase which is retained even at room temperature (Miyatani 1960). In this study, we report a low-temperature route to synthesize phases of Ag_2S, Ag_2Te and $Ag_2S_{1-x}Te_x$ $(0{\cdot}1 \leqslant x \leqslant 0{\cdot}9)$ similar to the method (Kulifay 1962) for synthesizing transition metal tellurides. These materials have been characterized by elemental analysis, powder X-ray diffraction (PXD) and differential scanning calorimetry (DSC). The room temperature PXD patterns of these solid solutions resemble α-phases of either Ag_2S or Ag_2Te depending on their composition. Unlike the parent compounds, which on heating undergo a distinct first order α-β transition, the solid solutions show a similar but broad phase transition.

2. Synthesis and characterization

Silver sulphide was prepared by mixing the solutions of $AgNO_3(2 \times 10^2 \text{ mol dm}^{-3})$ and $CS(NH_2)_2(0{\cdot}1 \text{ mol dm}^{-3})$ in water and heating around 353 K with constant

stirring for 2–3 h. The resulting black precipitate of Ag_2S was filtered, washed with water followed by methanol and dried in air oven at about 373 K.

Silver telluride was prepared by dissolving tellurium powder (0·01 mol) in hot 1:1 nitric acid and water. The excess acid was neutralized with the desired quantity of dilute ammonia solution. This solution was then added to silver nitrate (0·2 mol dm^{-3}) solution. The resulting solution was slowly added with constant stirring to 500 ml of 10% hydrazine hydrate in water having a pH of 9 which was raised to 10 by adding dilute ammonia solution and heating around 353 K with constant stirring for about 8 h. The black coloured Ag_2Te formed was washed and dried as before.

Thiourea hydrolyses in water giving H_2S (Pass and Sutcliffe 1968) and Te in tellurous acid was reduced from $+4$ to -2 by the addition of hydrazine hydrate. The plausible reaction route for the formation of Ag_2S and Ag_2Te may then be written as,

$$S=C(NH_2)_2+2H_2O\rightarrow 2NH_3+H_2S+CO_2$$

$$2AgNO_3+H_2S\rightarrow Ag_2S+2HNO_3$$

$$2Ag^{+}+Te^{+4}+N_2H_4+OH^{-}\rightarrow Ag_2Te+N_2O+5H_2O.$$

A similar procedure was adopted for the preparation of solid solutions $Ag_2S_{1-x}Te_x$ ($0{\cdot}1 \leqslant x \leqslant 0{\cdot}9$). Solutions of thiourea, tellurous acid and silver nitrate were added in the molar ratio of $1-x:x:2$ to 500 ml of 10% hydrazine hydrate solution in water at pH equal to 10. A portion of these compounds were annealed around 473 K in evacuated (10^{-5} torr) sealed tubes. Both the unannealed and annealed samples were characterized by PXD and DSC. The room temperature PXD patterns were recorded on a JEOL JDX-8P/70 X-ray diffractometer with CuK_α ($\lambda = 1{\cdot}5418$ Å) radiation. While the high temperature PXD patterns were obtained using a locally fabricated high temperature cell attached to PW 1050/70 Phillips X-ray diffractometer. The phase transformation temperature of the solid solutions were recorded on a Perkin Elmer DSC-2 differential scanning calorimeter.

3. Results and discussion

The elemental analysis showed a slight excess of Ag in all the solid solutions and hence only the nominal compositions are reported. The indexed room temperature PXD patterns of unannealed Ag_2S, Ag_2Te and two representative solid solutions $Ag_2S_{1-x}Te_x$ ($x = 0{\cdot}2$ and $0{\cdot}8$) are shown in figures 1 and 2 and their indexed patterns with relative intensities are given in tables 1 and 2, respectively. The PXD patterns of Ag_2S and Ag_2Te match with the respective monoclinic α-phases, whereas their solid solutions with compositions $x < 0{\cdot}3$ are similar to α-Ag_2S phase and those of compositions $x > 0{\cdot}6$ are akin to α-Ag_2Te phase. In the intermediate range ($x = 0{\cdot}4$, $0{\cdot}5$), the products are mixtures of α-Ag_2S and α-Ag_2Te phases.

From tables 3 and 4, it is seen that within a system the lattice parameters of the solid solutions do not vary much in relation to their parent compounds although the atomic sizes of S(1·27 Å) and Te(1·60 Å) do differ. However, the solid solutions have different phase transition temperatures as seen from figure 3. The phase transformation temperatures of the parent compounds are in agreement with the values reported in the literature (Miyatani 1959). The phase transition temperature of the solid solutions continuously varies on the tellurium and sulphur-rich sides.

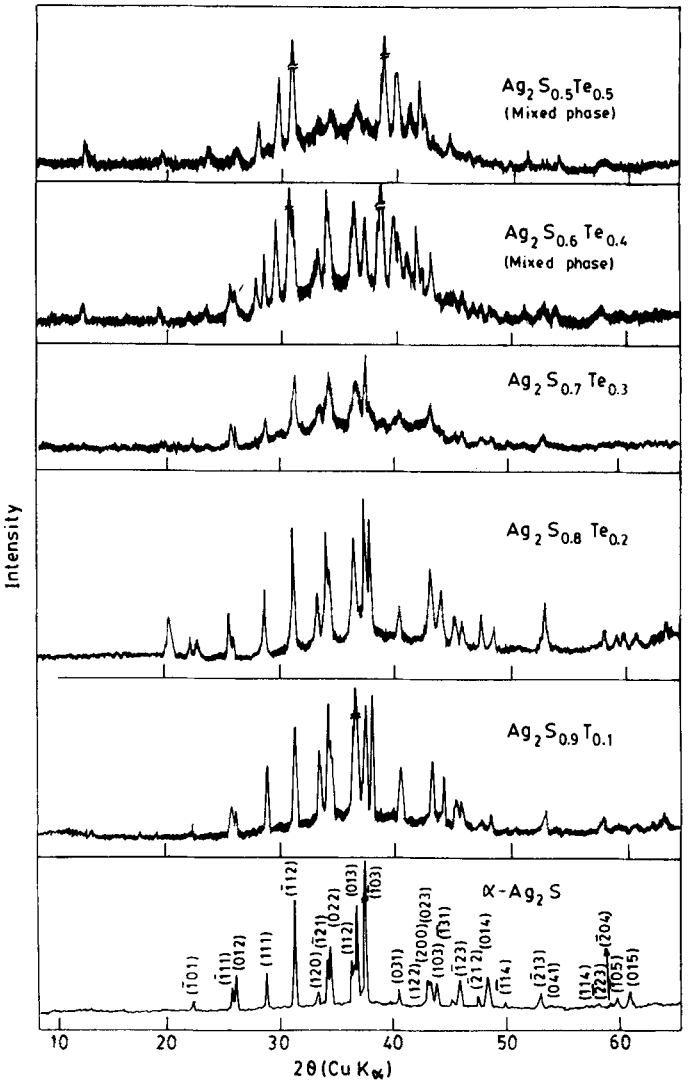

Figure 1. X-ray powder diffraction patterns of unannealed α-Ag_2S and solid solutions $Ag_2S_{1-x}Te_x (x \leq 0{\cdot}5)$.

Furthermore, all these phase transitions are reversible but are not as sharp as the parent compounds. It is interesting to note that the solid solution with $x = 0{\cdot}4$ shows only one phase transition, while the composition $x = 0{\cdot}5$ gives almost negligible enthalpy of phase transformation though mixtures of two phases are seen to be present in both the cases in their powder X-ray diffractograms.

Figure 4 shows the high temperature (523 K) PXD patterns of Ag_2S and Ag_2Te along with the four representative solid solutions. Of these the Ag_2S and Ag_2Te diffractograms resemble the bcc and fcc phases as reported in the powder diffraction files of inorganic compounds (4–0774 and 6–0575), while all the solid solutions but for $x = 0{\cdot}2$ show an amorphous diffraction pattern. However, the solid solutions on cooling show poor crystallinity.

Table 1. Indexed X-ray lines of Ag_2S and $Ag_2S_{0.8}Te_{0.2}$ (refined by least square method).

	Ag_2S			$Ag_2S_{0.8}Te_{0.2}$		
hkl	d_{obs}	d_{cal}	I_{obs}	d_{obs}	d_{cal}	I_{obs}
				4·291	—	26
$\bar{1}01$	3·952	3·953	4	3·952	3·960	16
				3·850		14
$\bar{1}11$	3·440	3·434	10	3·434		32
012	3·389	3·388	17	3·376	3·378	14
111	3·079	3·080	17	3·079	3·078	46
$\bar{1}12$	2·840	2·837	53	2·886	2·837	88
—	2·683	2·644	2			
120	2·667	2·664	6	2·663	2·664	35
—	2·644	—	2			
$\bar{1}21$	2·607	2·606	22	2·607	2·607	79
022	2·582	2·586	29	2·585	2·581	50
121				2·442	2·440	69
112	2·458	—	22			
013	2·426	2·425	48	2·426	2·417	48
$\bar{1}03$	2·383	2·384	100	2·385	2·380	100
—	2·257	—	3			
031	2·214	2·215	8	2·214	2·214	23
122	2·094	2·095	4			
200	2·085	2·081	13	2·085	2·085	51
023	2·076	2·074	12			
103	2·051	2·051	10	2·045	2·045	37
$\bar{1}31$	1·991	1·995	4	1·994	1·995	16
$\bar{1}23$	1·965	1·964	12	1·967	1·962	16
212	1·903	1·901	6	1·903	1·903	24
014	1·870	1·870	14	1·868	1·863	14
$\bar{1}14$	1·817	1·818	3			
$\bar{2}13$	1·719	1·717	8	1·717	1·718	33
041	1·692	1·692	2			
114	1·610	1·612	1			
$\bar{1}41$	1·585	1·587	1			
$\bar{2}23$	1·579	1·578	3	1·580	1·579	14
$\bar{2}04$	1·552	1·550	2	1·555	1·555	12
$\bar{1}05$	1·542	1·542	6	1·541	1·538	10
015	1·517	1·516	8	1·514	1·510	14
$\bar{1}34$				1·459	1·458	13
				—	—	22

The PXD patterns and the phase transition temperatures of the annealed samples of the parent compounds and their solid solutions of compositions $x = 0{\cdot}1$ and $0{\cdot}8$ are the same as of the unannealed sample. For the intermediate compositions ($x = 0{\cdot}4 - 0{\cdot}6$), diffused patterns were observed similar to the one reported by Koji and Iida (1985) for the samples prepared by conventional solid-state reactions. For the compositions $x = 0{\cdot}2$, $0{\cdot}3$ and $0{\cdot}7$, the PXD patterns are poorly crystalline with a broad phase transition as shown in figure 5.

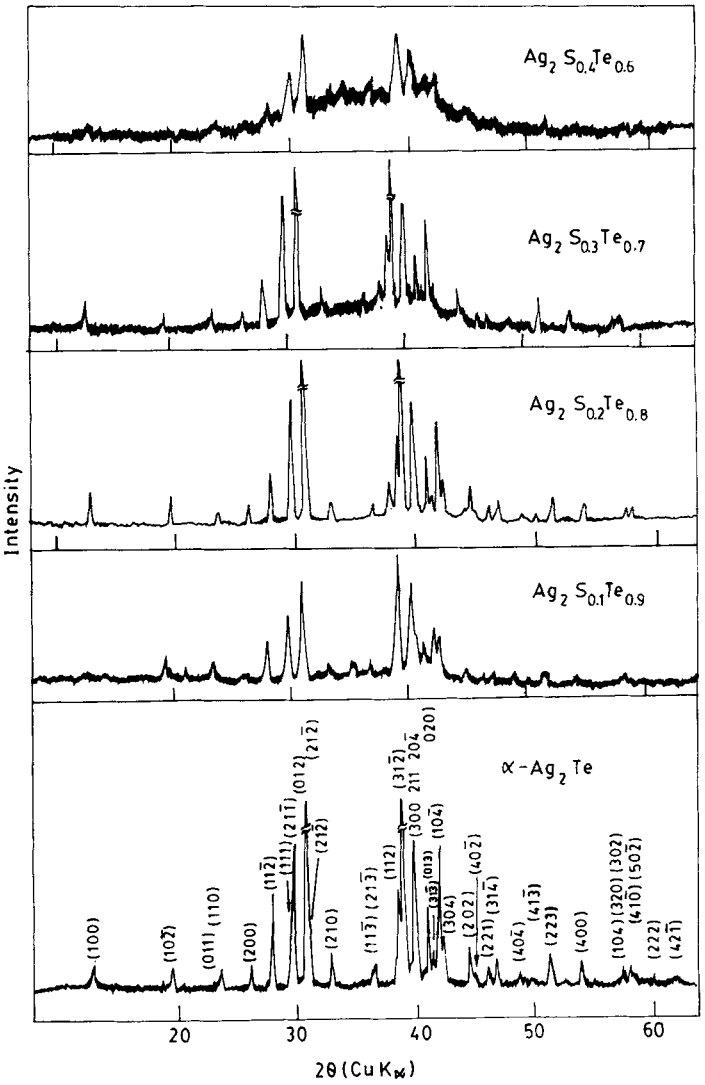

Figure 2. X-ray powder diffraction patterns of unannealed α-Ag_2Te and solid solutions $Ag_2S_{1-x}Te_x (x \geqslant 0{\cdot}6)$.

Table 2. Indexed X-ray lines of Ag_2Te and $Ag_2S_{0{\cdot}2}Te_{0{\cdot}8}$.

	Ag_2Te			$Ag_2S_{0{\cdot}2}Te_{0{\cdot}8}$		
hkl	d_{obs}	d_{cal}	I_{obs}	d_{obs}	d_{cal}	I_{obs}
100	6·810	6·779	11	6·733	6·760	13
$10\bar{2}$	4·495	4·489	8	4·484	4·484	10
$11\bar{1}$	3·834	3·840	3	—	3·836	—
002	—	—	—	3·754	3·758	5
110	3·739	3·742	7	3·723	3·734	6

(*Continued*)

Table 2. (*Continued*)

	Ag_2Te			$Ag_2S_{0.2}Te_{0.8}$		
hkl	d_{obs}	d_{cal}	I_{obs}	d_{obs}	d_{cal}	I_{obs}
200	3·389	3·389	10	3·700	3·380	9
$11\bar{2}$	3·175	3·174	29	3·159	3·168	24
111	3·013	3·007	40	—	3·000	—
$21\bar{1}$	2·993	2·995	62	2·979	2·986	57
012	2·880	2·881	100	—	2·879	—
$21\bar{2}$	2·858	2·870	30	2·867	2·858	100
210	2·698	2·706	14	2·691	2·698	9
$11\bar{3}$	2·452	2·452	9	2·447	2·449	6
$21\bar{3}$	2·445	—	—	—	2·440	
—	—	—	—	2·359	—	16
112	2·324	2·324	44	2·315	2·322	35
$31\bar{2}$	2·308	2·309	100	2·295	2·301	85
300	—	2·261	—	—	2·253	
211	2·254	2·251	64	—	2·248	
$20\bar{4}$		2·245	—	2·242	2·240	54
020	—	2·240	—	—	2·240	
013	2·189	2·188	36	2·186	2·187	28
$31\bar{3}$	2·171	2·174	16	2·166	2·167	8
021	—	2·147	—	—	2·147	—
121	2·145	2·145	60	—	2·145	
$10\bar{4}$	—	2·136	—	2·137	2·135	45
$30\bar{4}$	2·125	2·125	23	2·117	2·118	16
	—	—	—	2·041	—	4
202	2·025	2·026	16	2·026	2·024	16
$40\bar{2}$	2·010	2·007	3	2·006	2·003	4
$22\bar{1}$	1·961	1·960	6	1·957	1·957	7
$11\bar{4}$	1·935	1·929	10	—	1·927	
$31\bar{4}$	—	1·920	—	1·927	1·915	10
$40\bar{4}$	1·864	1·864	5	1·855	1·856	4
—	—	—	—	1·852	—	1
113	1·850	1·841	3	1·841	1·840	1
$41\bar{3}$	1·826	1·827	4	1·817	1·820	3
$12\bar{3}$	1·779	1·779	14	—	1·778	—
$22\bar{3}$	—	1·777	—	1·771	1·775	11
014	1·738	1·733	3	1·734	1·173	8
—	—	—	—	1·728	—	1
$32\bar{1}$	—	1·694		1·692	1·691	8
400	1·695	1·695	10	—	1·690	
104	1·604	1·600	5	1·600	1·600	4
410	1·587	1·586	8	1·585	1·582	4
$50\bar{2}$	—	1·581	—	1·575	1·575	1
$12\bar{4}$	—	1·546	—	—	1·545	—
324	—	1·542	—	1·538	1·540	1
114	1·512	1·507	2	1·506	1·507	1
222	1·502	1·503	3	1·499	1·502	1

(*Continued*)

Table 2. (*Continued*)

	Ag_2Te			$Ag_2S_{0.2}Te_{0.8}$		
hkl	d_{obs}	d_{cal}	I_{obs}	d_{obs}	d_{cal}	I_{obs}
$42\bar{2}$	—	1·497	—	—	1·493	
$30\bar{6}$	—	1·497	—	—	1·493	
$51\bar{4}$	—	1·495	—	—	1·488	
321	1·448	1·448	15	1·443	1·446	13
$42\bar{1}$	—	1·445	—	—	1·441	
—	—	—	—	1·408	—	1
$22\bar{5}$	—	1·395	—	1·397	1·394	12
032	—	1·388	—	1·391	1·389	10

Table 3. Lattice parameters of Ag_2S and solid solutions $Ag_2S_{(1-x)}Te_x$ ($x \leqslant 0{\cdot}3$).

Compound	*a* (Å)	*b* (Å)	*c* (Å)	β	Cell vol (Å^3)	Density (d/g cm^{-3})
Ag_2S	4·222(9)	6·93(2)	7·88(0)	99·58(8)	227·34	7·239
$Ag_2S_{0.9}Te_{0.1}$	4·23(3)	6·93(6)	7·92(7)	100·1(4)	228·57	7·478
$Ag_2S_{0.8}Te_{0.2}$	4·23(2)	6·93(4)	7·85(4)	99·7(1)	226·82	7·815
$Ag_2S_{0.7}Te_{0.3}$	4·23(3)	6·94(4)	7·86(5)	99·9(2)	227·37	8·075

Table 4. Lattice parameters of Ag_2Te and solid solutions $Ag_2S_{(1-x)}Te_x$($x \geqslant 0{\cdot}6$).

Compound	*a* (Å)	*b* (Å)	*c* (Å)	β	Cell vol (Å^3)	Density (g cm^{-3})
Ag_2Te	8·10(2)	4·488(9)	8·98(2)	123·15(7)	273·32	8·343
$Ag_2Te_{0.9}S_{0.1}$	0·07(3)	4·47(2)	8·94(3)	123·0(7)	270·46	8·196
$Ag_2Te_{0.8}S_{0.2}$	8·10(2)	4·488(9)	8·98(2)	123·0(1)	273·78	7·875
$Ag_2Te_{0.7}S_{0.3}$	8·08(2)	4·47(2)	8·97(3)	123·04(9)	270·98	7·646
$Ag_2Te_{0.6}S_{0.4}$	8·08(2)	4·47(1)	8·97(3)	123·25(7)	270·94	7·414

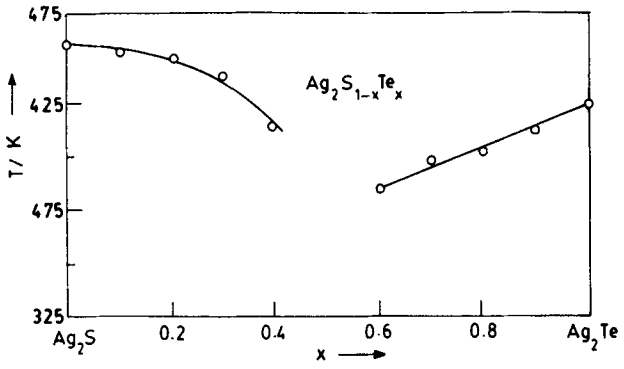

Figure 3. Phase transition temperature of Ag_2S and Ag_2Te and their solid solutions $Ag_2S_{1-x}Te_x$ as a function of *x*.

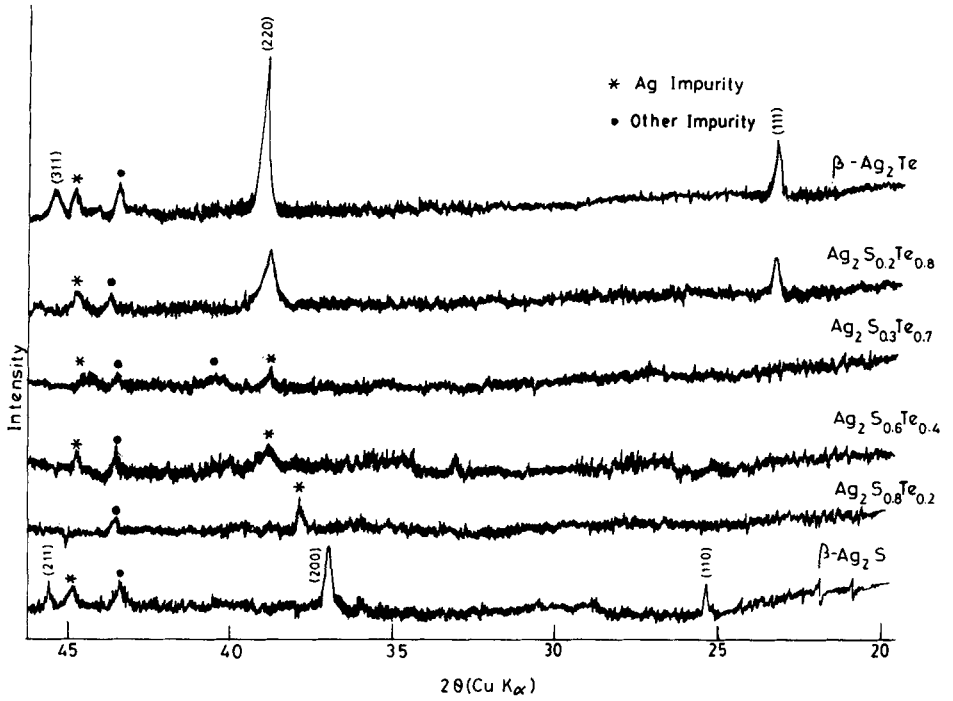

Figure 4. X-ray powder diffraction patterns of β-Ag_2S, β-Ag_2Te and $Ag_2S_{1-x}Te_x$ at 523 K.

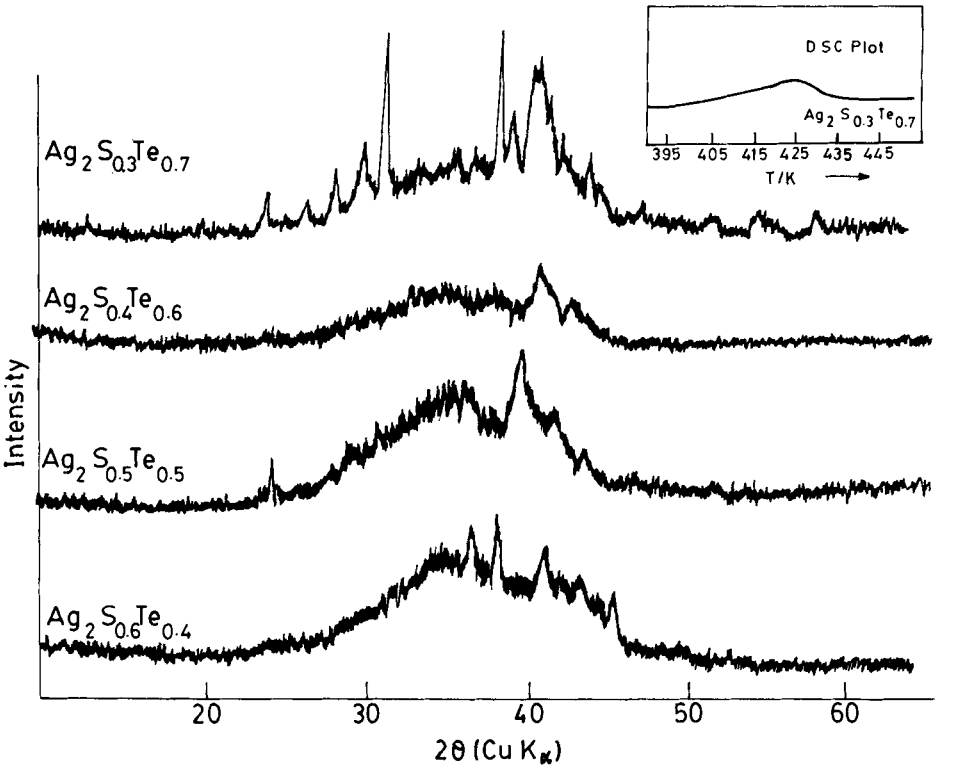

Figure 5. X-ray powder diffraction patterns of annealed $Ag_2S_{1-x}Te_x$ ($x = 0{\cdot}4 - 0{\cdot}7$); the inset shows a typical DSC curve for the solid solution of $x = 0{\cdot}7$.

References

Koji H and Iida K 1985 *J. Phys. Soc. Jpn* **54** 2218
Kulifay M S 1962 *J. Am. Chem. Soc.* **83** 4961
Miyatani S 1958 *J. Phys. Soc. Jpn* **13** 341
Miyatani S 1959 *J. Phys. Soc. Jpn* **14** 1634
Miyatani S 1960 *J. Phys. Soc. Jpn* **15** 1586
Pass G and Sutcliffe H 1968 *Practical inorganic chemistry* (London: Chapman and Hall)
Shukla A K and Schmalzried H 1979 *Z. Phys. Chem.* **59** 118
Shukla A K, Vasan H N and Rao C N R 1981 *Proc. R. Soc.* (*London*) **A376** 619
Sohege J and Funke K 1984 *Ber. Bunsenges. Phys. Chem.* **88** 657
Sohege J and Funke K 1989 *Ber. Bunsenges. Phys. Chem.* **93** 115
Wagner C 1953 *J. Chem. Phys.* **21** 1819