Stable and Metastable Phases in the Systems AgI-Ag_2XO_4 (X=Cr, Mo, W)

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DTA and powder x-ray diffraction measurements allowed to draw the phase diagrams of the systems $AgI-Ag_2XO_4$ (X=Cr, Mo, W).

A more detailed investigation was devoted to the composition range around $X_{AgI}=0.8$, where in preliminary tests it was observed that the room temperature ionic conductivity strongly depends on the thermal treatment of the sample.

By quenching mixtures at $X_{AgI}=0.8$, glass-like phases with high conductivity were obtained; in the systems $AgI-Ag_2CrO_4$ and $AgI-Ag_2Mo_4$ the subsequent crystallization gave rise to non conducting phases, whereas the occurrence of the highly conducting compound $4\,AgI\cdot Ag_2WO_4$ was recognized in the third system investigated.

Introduction

Many papers were recently devoted to investigations of solid electrolytes containing AgI which show high ionic conductivity at room temperature. Noteworthy results were obtained for the systems $AgI-Ag_nXO_4$ and $AgI-Ag_nX_2O_4$ (X = W, Cr, Mo, P, V, Te, Se, As) [1–6].

In a previous work by our group [2], electric a. c. conductivity and e. m. f. determinations were carried out on solid electrolytes formed with AgI and Ag_2XO_4 (X = Cr, Mo, W) of a composition close to 80 mole% AgI. These electrolytes, prepared by quenching of the corresponding molten mixtures, showed an electric conductivity at 23 °C as large as $10^{-2}\ \Omega^{-1}\,cm^{-1}$. In preliminary tests, transport number determinations (Tubandt's method) allowed to establish that the silver ions are the only carriers in these materials.

Furthermore it was observed that, after annealing at $T>80$ °C, the original materials, excepted the case of the $AgI-Ag_2WO_4$ system, showed a much lower conductivity at room temperature (Figure 1).

In order to attain a more detailed information about such high conducting phases, in the present work the phase diagrams of these systems were defined through DTA and x-ray diffraction determinations on samples subjected to different thermal treatments.

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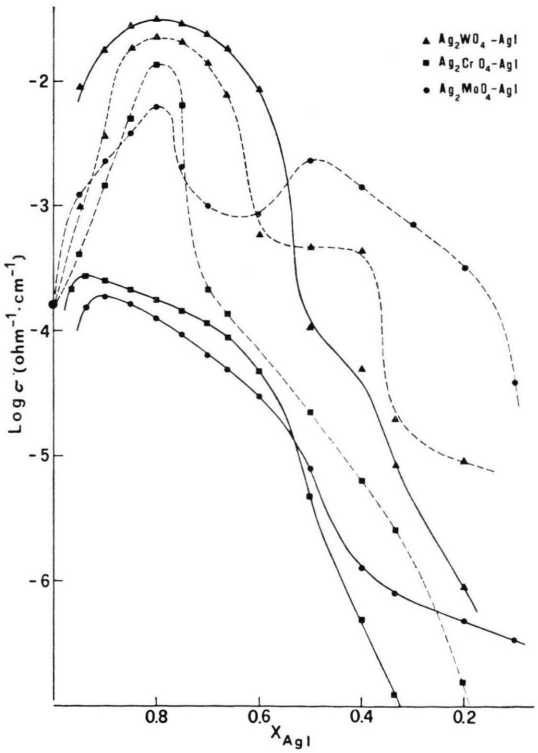

Fig. 1. Electrical conductivity at 23 °C vs. composition in the systems $AgI-Ag_2XO_4$ (X = Cr, Mo, W). Data concern quenched (dashed lines) and annealed (full lines) samples; the arrangement of the conductivity cells and the instrumental apparatus are reported in a previous work [2].

Experimental

Fluka puriss. AgI and Ag_2CrO_4 were directly employed, whereas Ag_2MoO_4 and Ag_2WO_4 were precipitated from aqueous C. Erba RP $AgNO_3$ with C.

Erba RP Na_2MoO_4 or BDH Analar Na_2WO_4 and then thoroughly washed and dried at 120 °C under vacuum and protected from light.

Salt mixtures with different compositions were heated in a sealed quartz tube at 100 °C above the melting point, then quenched in liquid N_2 and grinded.

For DTA determinations a Du Pont "900 DSC" was employed; 100 mg powder samples were sealed in silver caps; carborundum was used as reference; the heating rate generally was 10 deg·min^{-1}.

X-ray diffraction patterns of powdered salts were obtained at room temperature with the Cu Kα radiation in the Philips camera PW 1011/00 working at 18 mA and 40 kV.

Results and Discussion

DTA and x-ray results concern samples which had been subjected to either quenching from 100 °C above the melting point (i. e. in the same conditions which gave high conducting materials [2]) or annealing one week at 20 °C below the eutectic temperature.

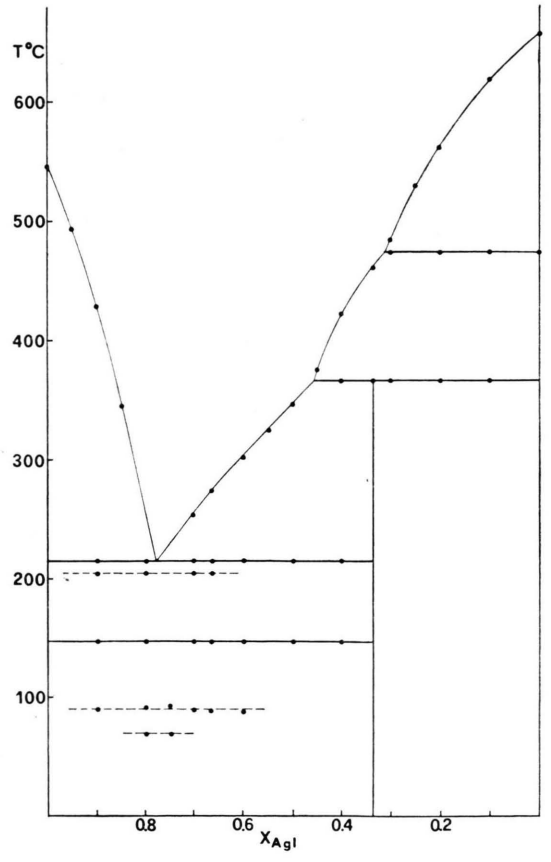

Fig. 2 a. Phase diagram of the system $AgI-Ag_2CrO_4$.

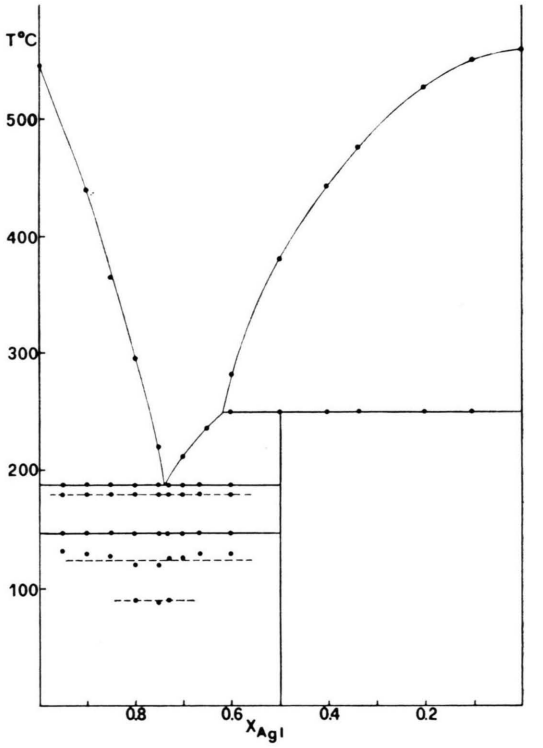

Fig. 2 b. Phase diagram of the system $AgI-Ag_2MoO_4$.

The phase diagrams of the three systems studied are shown in Fig. 2 a, 2 b, and 2 c, where the dashed and full lines refer to the quenched and annealed samples respectively.

As for the annealed samples, the following results were obtained.

System $AgI-Ag_2CrO_4$ (Fig. 2 a): a eutectic at $X_{AgI}=0.78$, $T=215$ °C and an incongruent compound $AgI\cdot 2\,Ag_2CrO_4$ decomposing at 367 °C; Ag_2CrO_4 (m.p. 657 °C) shows a phase transition at 474 °C. System $AgI-Ag_2MoO_4$ (Fig. 2 b): a eutectic at $X_{AgI}=0.74$, $T=188$ °C and an incongruent compound $AgI\cdot Ag_2MoO_4$ decomposing at 250 °C; Ag_2MoO_4 melts at 558 °C.

System $AgI-Ag_2WO_4$ (Fig. 2 c): a eutectic at $X_{AgI}=0.75$, $T=297$ °C and two incongruent compounds, $4\,AgI\cdot Ag_2WO_4$ and $AgI\cdot 2\,Ag_2WO_4$, which decompose at 308 and 364 °C respectively; Ag_2WO_4 (m.p. 604 °C) shows a phase transition near the melting point (592 °C). The data concerning this system are in agreement with the phase diagram by Takahashi [1].

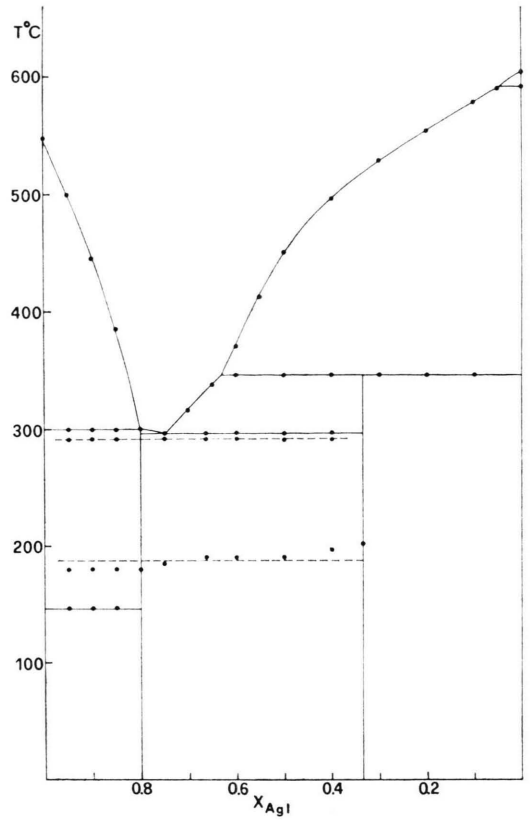

Fig. 2 c. Phase diagram of the system $AgI-Ag_2WO_4$.

The occurrence of the mentioned intermediate compounds is supported by the x-ray diffraction patterns obtained from annealed samples and reported in Table 1.

DTA and x-ray diffraction data taken on quenched samples are remarkably different from those taken on the annealed ones, particularly in the case of the AgI rich compositions.

For a wide composition range around the eutectic points, the $AgI-Ag_2CrO_4$ and $AgI-Ag_2MoO_4$ quenched samples showed two exothermic effects: the first, quite diffuse at 70 – 90 °C, the second, more evident at 100 – 120 °C (Figure 3 a). The latter attained the largest intensity at a composition close to $X_{AgI}=0.8$. Such effects are represented in the phase diagrams by dashed lines (Fig. 2 a and 2 b). No effect of this kind was detected in any annealed samples (Figure 3 b).

A detailed investigation was devoted to the study of the thermal effect related to the $\beta \rightarrow \alpha$ transition of AgI at 147 °C. It was observed that in the systems containing Ag_2CrO_4 and Ag_2MoO_4 the amount of AgI undergoing the transition, which was estimated through a quantitative determination of the corresponding DTA peak area, which obviously is 100% for pure AgI, decreases according to the expected law for a diphasic mixture of AgI and the intermediate compound reported in the corresponding phase diagram, whereas for the quenched samples the DTA peak area is always smaller than for the annealed ones (Fig. 4 a and 4 b). As for the system $AgI-Ag_2WO_4$, the thermograms show no exothermic peaks before the AgI phase transition,

Table 1. Powder x-ray patterns for the systems $AgI-Ag_2CrO_4$, $AgI-Ag_2MoO_4$, and $AgI-Ag_2WO_4$ (only the most intensive signals are reported).

Ag_2CrO_4		$AgI \cdot 2\,Ag_2CrO_4$		AgI	
d(Å)	I	d(Å)	I	d(Å)	I
2.87	100	5.18	25	3.75	100
2.85	90	2.78	70	2.30	70
2.77	50	2.74	100	1.96	40
2.05	20	2.42	40		
1.99	20	2.26	25		

Ag_2MoO_4		$AgI \cdot Ag_2MoO_4$	
d(Å)	I	d(Å)	I
3.29	25	3.67	20
2.81	100	3.18	100
2.69	25	3.07	20
2.33	20	3.01	20
1.79	40		
1.65	40		

Ag_2WO_4		$4\,AgI \cdot Ag_2WO_4$		$AgI \cdot 2\,Ag_2WO_4$	
d(Å)	I	d(Å)	I	d(Å)	I
2.96	12	3.68	70	3.05	30
2.84	100	3.46	100	2.99	100
2.72	20	2.75	80	2.86	60
2.01	30	2.56	80	2.81	50

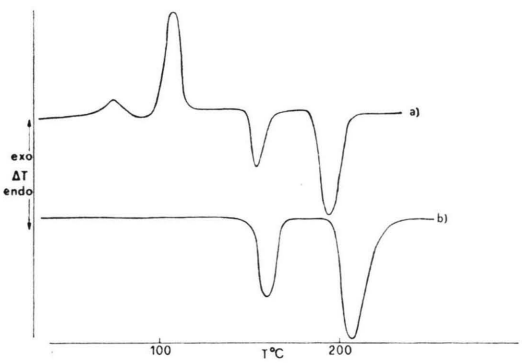

Fig. 3. Typical DTA patterns for samples with AgI rich composition: a) quenched, b) annealed.

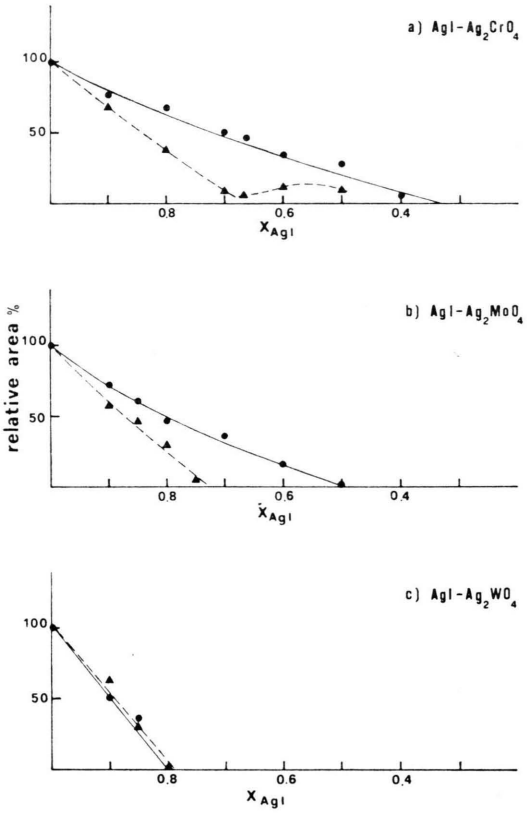

Fig. 4. Relative DTA peak areas of the $\beta \rightarrow \alpha$ AgI transition (147 °C) vs. composition in the systems: a) $AgI-Ag_2CrO_4$, b) $AgI-Ag_2MoO_4$, c) $AgI-Ag_2WO_4$.

while a single peak (exothermic) appears at about 190 °C. The area underlying the 147 °C peak for quenched samples is generally as large as for the annealed ones and vanishes for both kinds of treatment at $X_{AgI}=0.8$ (Figure 4 c).

Another difference between quenched and annealed samples is an endothermic peak which can be observed only in the former ones just below (5 – 10 °C) the eutectic point.

The occurrence of the exothermic signals in the quenched samples thermograms (Fig. 3 a) might be compared with the typical thermograms obtained from amorphous materials [7]. Accordingly, the first thermal effect would correspond to the glass transition temperature, whereas the second exothermic peak would be due to crystallization.

Investigation by means of the microscope confirms this hypothesis particularly for the system $AgI-Ag_2MoO_4$, where apparent softening phenomena of the quenched materials, observed at about 80 °C, are followed by a crystallization process at higher temperature (≈ 120 °C).

A more direct support is obtained from the x-ray analysis carried out, at room temperature, on quenched samples. Indeed, the results concerning the range of the compositions richer in AgI were similar to those reported by Kunze for $AgI-Ag_2SeO_4$ [5]. The patterns show only peaks due to γ-AgI, the intensities of which decrease with the AgI content and vanish at $X_{AgI}=0.8$. For the composition $X_{AgI}=0.8$ only a few diffuse bands are observed which might be interpreted as due to an amorphous substance. In the case of the system $AgI-Ag_2WO_4$ the observed patterns were quite complex. At $X_{AgI}=0.8$ very weak signals were detected at the same position of more intense ones already attributed to the compound $4\,AgI\cdot Ag_2WO_4$ in the annealed samples; at $X_{AgI}=0.66$ a few signals were also observed which cannot be reliably referred to any of the identified phases and might be attributed to the compound $2\,AgI\cdot Ag_2WO_4$ reported by Takahashi [1].

On the basis of the above results one may conclude that, at least for the systems $AgI-Ag_2CrO_4$ and $AgI-Ag_2MoO_4$, the quenched mixtures at $X_{AgI}=0.8$ are substantially metastable amorphous phases; accordingly, the time dependent decrease of the conductivity observed at $T>60$ °C [4] might be due to a crystallization process which allows the formation of low conducting phases, i. e. AgI and $AgI\cdot Ag_2CrO_4$ or $AgI\cdot Ag_2MoO_4$. As for the system $AgI-Ag_2WO_4$, the general similarity between the behaviour of quenched and annealed samples at $X_{AgI}=0.8$ might be explained assuming that the higly conducting compound $4\,AgI\cdot Ag_2WO_4$ is formed, the conductivity of which rises with rising temperature [2] and takes time independent values up to the melting point.

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[7] See e. g.: Wilbur and Dowson in "Differential Thermal Analysis", vol. II, Ed. Mackenzie, p. 237; D. D. Thornburg, Mat. Res. Bull. **9**, 1481 [1974].