JOURNAL OF SOLID STATE CHEMISTRY **140,** 91–96 (1998)
ARTICLE NO. SC987867

Devitrification and Metastability: Revisiting the Phase Diagram of the System AgI : Ag_2MoO_4

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Received September 29, 1997; in revised form April 21, 1998; accepted April 30, 1998

The phase diagram of the $AgI_{(1-x)}(Ag_2MoO_4)_x$ system has been investigated by differential scanning calorimetry (DSC) and X-ray powder diffraction (XRD). Besides an incongruent 1 : 1 compound that was previously reported by our group, a metastable 2 : 1 crystalline phase is formed at ~110°C over the whole composition range. The stability of this phase is strongly temperature-controlled: at ~180°C the crystal decomposes in the time scale of a DSC experiment. For $x < 0.5$ it gives β-AgI and the 1 : 1 compound, whereas for $x > 0.5$ the 1 : 1 and Ag_2MoO_4 are formed. The glass-forming region spans over the range $0.20 < x < 0.40$. Annealing the samples with $0 \leq x < 0.33$ near 70°C causes all AgI in excess with respect to the 2 : 1 compound to crystallize as β phase. © 1998 Academic Press

1. INTRODUCTION

Fast ion conducting (FIC) glasses have been widely studied for their potential as electrolytes in solid state electrochemical devices like batteries and sensors. In particular, at room temperature silver-based glasses display conductivity values of the order of 10^{-2} ohm^{-1}cm^{-1} (1).

The pseudobinary system $(AgI)_{(1-x)}(Ag_2MoO_4)_x$ gives glasses in the range $0.2 < x < 0.4$. Its structural, transport, and thermal properties were studied earlier by Japanese groups (2–7). The equilibrium phase diagram over the whole composition range was sketched by our group during the 1970s (8). We found a eutectic for $x \cong 0.25$ at $T \cong 180$°C and a subsequent peritectic at 240°C which corresponds to the formation of the AgI : Ag_2MoO_4 (1 : 1) compound ($x = 0.5$). However, at that time some detail were not fully understood: in particular, the molar enthalpies of the $\beta \rightarrow \alpha$ transition of AgI at 147°C displayed different behaviors against the compositional parameter, x, in as-quenched and annealed samples.

Recently, AgI : Ag_2MoO_4 glasses have gained renewed interest as a model system for structural studies of disordered materials. Swenson *et al.* (9) showed by X-ray and neutron diffraction in conjunction with the reverse Montecarlo technique that no polymerization takes place, unlike what happens in phosphate and borates.

The existence of complex relationships among devitrification processes and glass transport properties has been pointed out. Maier *et al.* (10) showed that it is possible to retain at room temperature the high conductivity level displayed by silver-based glasses above the glass transition, T_g. These results are important both from the basic and the technological points of view, so we decided to revisit our phase diagram by devoting more attention to the metastability and the approach toward the equilibrium. In this paper we present our new conclusions obtained by means of DSC and X-ray diffraction.

2. EXPERIMENTAL

2.1. Sample Preparation

Glassy or partially glassy samples of the $(AgI)_{1-x}(Ag_2MoO_4)_x$ system (with $x = 0.1$, 0.2, 0.25, 0.33, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9) were prepared by the melt–quenching technique. Appropriate mixtures of AgI (Aldrich 99%) and Ag_2MoO_4 (prepared by precipitation from aqueous solution of $AgNO_3$ and Na_2MoO_4 (11)) were melted at 600°C for 2 h in quartz tubes and then quenched down to room temperature in stain steel moulds.

2.2. Annealing Procedures

Samples in the whole composition range were treated at different temperatures, according to DSC scans previously performed on "as-quenched" specimens. In fact, the annealing temperatures were chosen just above the last exothermic peak in order to let the samples reach the equilibrium.

Aliquots of samples having $x \leq 0.4$ were annealed at 140°C for 30 min, whereas aliquots of samples with $x \geq 0.5$ were first treated at 210°C for 30 min and then at 130°C for 30 min. No samples show evidence of either T_g or cold crystallization after treatments.

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0022-4596/98 $25.00

In order to better investigate the devitrification processes, further annealing was made on some samples: aliquots of $x = 0.25, 0.33$, and 0.5 were treated at 70°C for 15 h; aliquots of $x = 0.33$ and 0.5 were also treated at 140°C for 15 h and 3 days and at 160°C for 15 h.

2.3. Apparatus

Differential scanning calorimetry measurements (DSC) were run with a 2910 DSC controlled by a TA 2000 system (TA Instruments). All experiments were performed on powdered samples, in crimped silver pans, at a rate of 10°C/min under dry N_2 purge. The temperatures of the thermal phenomena are affected by an uncertainty of ± 2°C.

Powder X-ray diffraction patterns were taken on a Philips PW 1710 powder diffractometer, equipped with a Philips PW 1050 vertical goniometer and a graphite crystal monochromator (Cu$K\alpha$ radiation).

3. RESULTS

3.1. As-Quenched Samples

Figure 1 reports the DSC thermograms from room temperature up to 200°C of $x = 0.25$ (a) and $x = 0.33$ (b) as-quenched samples. In curve (a) one can observe a baseline change at 50°C which corresponds to the glass transition, an exothermic peak at about 80°C, which can be ascribed to the crystallization of AgI (see below), and a larger exothermic effect at 110°C followed by an endothermic peak at 148°C, which is attributed to the AgI $\beta \rightarrow \alpha$ transition, and by a double peak at 175°C. Curve (b) presents T_g at 50°C, an exothermic peak at 110°C, and an endothermic peak at 180°C. Neither the exothermic peak at 80°C nor the $\beta \rightarrow \alpha$ transition at 148°C is present.

The DSC analyses performed on all as-quenched samples always show the presence of glassy phases. In particular, samples with $x = 0.1$ and 0.2 exhibit a thermal behavior very close to that of $x = 0.25$ sample (curve a).

X-ray powder diffraction patterns of as-quenched samples were collected for all the investigated compositions. Samples for $0.20 < x < 0.40$ do not show diffraction peaks and belong to the glass-forming region, in agreement with the data of Minami and co-workers (4). Samples $x = 0.10$ and 0.20 show the pattern of β-AgI, whereas compositions with $x \geq 0.4$ show the peaks of Ag_2MoO_4.

3.2. Annealed Samples

Figure 2 shows the X-ray diffraction patterns of samples $x = 0.25$ (a) and $x = 0.33$ (b) treated at 70°C for 15 h. Pattern (a) presents some diffraction peaks that can be identified as β-AgI. On the contrary, pattern (b) does not evidence any crystalline phase.

Figure 3 reports the DSC thermograms of pure crystalline AgI (curve a) and of the samples $x = 0.25$ (b) and $x = 0.33$ (c) annealed at 140°C for 30 min. Crystalline AgI shows the $\beta \rightarrow \alpha$ transition at 148°C and the melting peak at 540°C (12). Curve (b) presents a small peak at 148°C and a larger one at 180°C. Curve (c) shows a sharp peak at 180°C which is immediately followed by a broader one starting at 190°C.

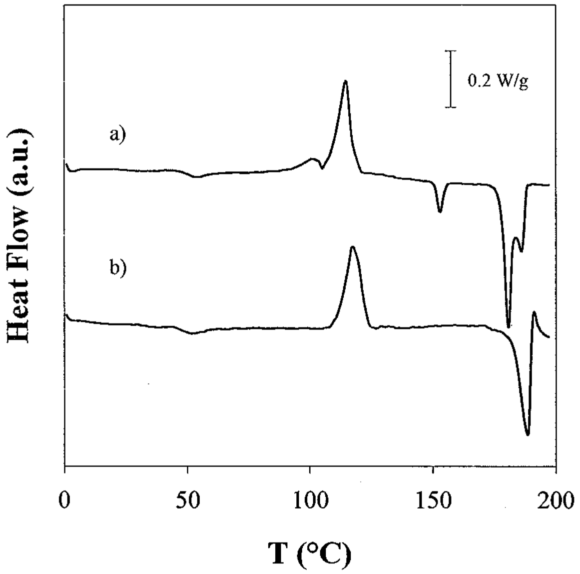

FIG. 1. DSC thermograms of (a) $x = 0.25$ and (b) $x = 0.33$ as-quenched glassy samples.

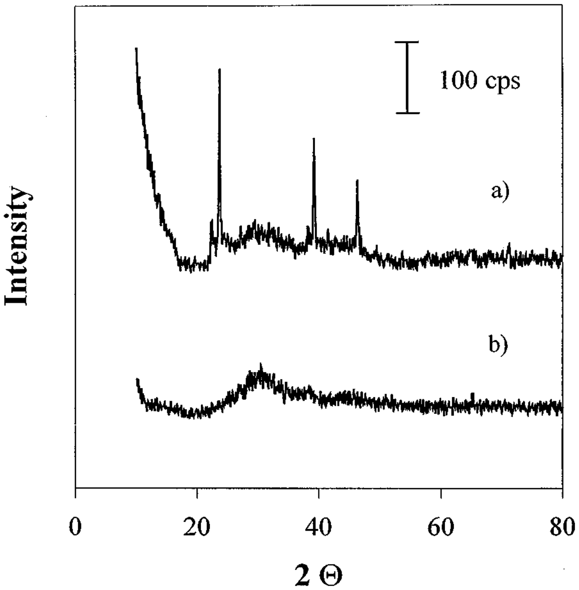

FIG. 2. X-ray diffraction patterns of (a) $x = 0.25$ and (b) $x = 0.33$ samples annealed at 70°C for 15 h.

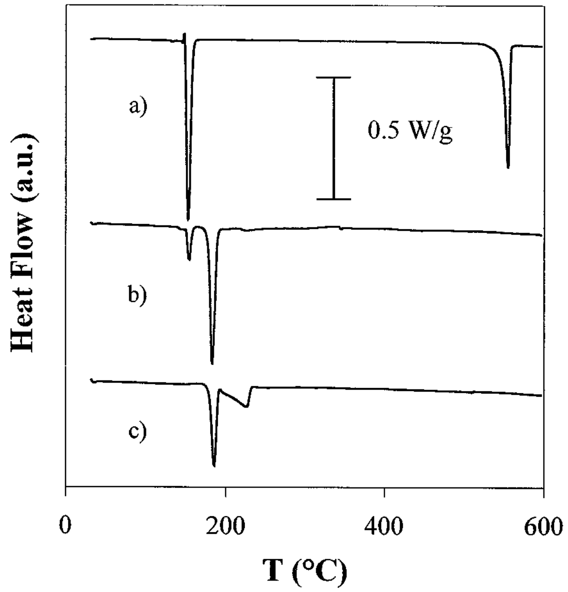

FIG. 3. DSC thermograms of (a) pure AgI, (b) $x = 0.25$, and (c) $x = 0.33$ samples. Samples (b) and (c) were annealed at 140°C for 30 min.

Figure 4 reports the DSC thermograms of $x = 0.50$ (curve a), $x = 0.70$ (curve b) annealed samples, and of pure crystalline Ag_2MoO_4. In curve (a) three sharp peaks are observed: a very small feature at 150°C is followed by another at 180°C and by a larger one at 240°C. A very broad thermal effect is also detected between 350 and 400°C. Curve (b) shows a sharp peak at 240°C followed by a broad thermal effect ranging between 350 and 550°C. Curve (c) represents the typical thermogram of silver molybdate: a small endothermic peak at 482°C which is related to the $\beta \rightarrow \gamma$ polymorphic transition, and the melting peak at 560°C (11).

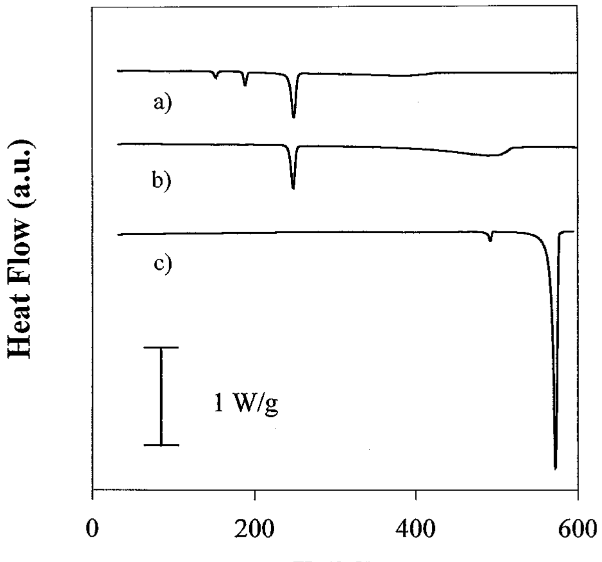

FIG. 4. DSC thermograms of (a) $x = 0.50$, (b) $x = 0.70$, and (c) pure Ag_2MoO_4. Samples (a) and (b) were annealed at 210°C for 30 min and then at 130°C for 30 min.

4. DISCUSSION

The DSC runs performed on as-quenched samples generally show an exothermic effect ranging between 110 and 130°C, that corresponds to the crystallization of an unknown phase. Figure 5 reports the crystallization enthalpy, ΔH_{cr}, as a function of composition: a maximum is found around $x = 0.33$. The experimental data are well fitted by the relationship

$$\Delta H_{cr}(x) = \Delta H_{cr}(x = 0.33)y, \qquad [1]$$

where $\Delta H_{cr}(x = 0.33) = 22.03\ \mathrm{J\ g^{-1}}$, and y is the maximum allowed weight fraction of 2AgI:Ag_2MoO_4 (2:1) compound, which is given by

$$y = \frac{x(2M_{AgI} + M_{Ag_2MoO_4})}{(1-x)M_{AgI} + xM_{Ag_2MoO_4}}, \quad \text{for } 0 \le x \le 0.33, \qquad [2]$$

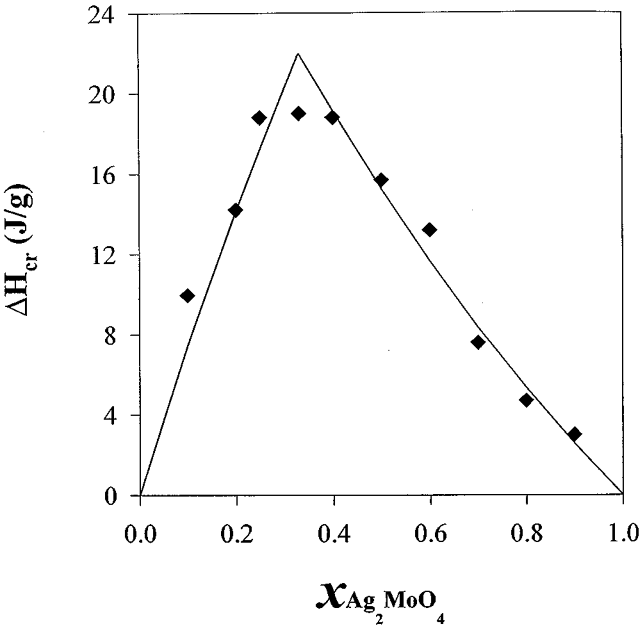

FIG. 5. Crystallization enthalpy, ΔH_{cr}, of the 2:1 compound vs the Ag_2MoO_4 molar fraction. The squares represent the experimental points, whereas the line gives the theoretical dependence described by Eqs. [1]–[3] (see text).

and by

$$y = \frac{1-x}{2}\frac{(2M_{\mathrm{AgI}} + M_{\mathrm{Ag_2MoO_4}})}{(1-x)M_{\mathrm{AgI}} + xM_{\mathrm{Ag_2MoO_4}}}, \quad \text{for } 0.33 \le x \le 1, \tag{3}$$

where M_{AgI} and $M_{\mathrm{Ag_2MoO_4}}$ are the molecular weights of the two starting compounds.

This result means that, over the whole composition range, the glassy phase tends to crystallize by yielding the maximum allowable fraction of the 2:1 compound. The thermal behaviors of as-quenched $x = 0.25$ and 0.33 samples reported in Fig. 1 [curves (a) and (b), respectively] also support the present conclusion. In fact, in $x = 0.25$ the excess of AgI with respect to the 2:1 composition crystallizes at about 80°C, as shown by the first exothermic peak of curve (a), whereas $x = 0.33$ shows no AgI crystallization peak.

The stability of 2:1 phase has been checked by X-ray powder diffraction on $x = 0.33$ samples annealed for 15 h at 140°C (Fig. 6a) and at 160°C (Fig. 6b). Pattern (a) does not present any peak which can be ascribed either to AgI or Ag_2MoO_4, and it is characteristic of the 2:1 phase. The pattern collected on the sample annealed at 160°C (b) shows the segregation of AgI and the slow growth of another crystalline phase, which can be ascribed to the 1:1 compound on the basis of our previous work (8). These results show that the 2:1 compound is metastable and undergoes a kinetically limited transformation into stable phases.

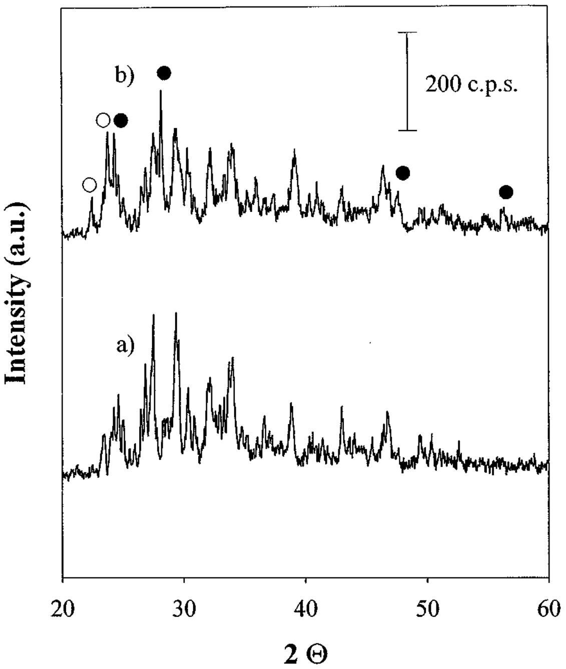

FIG. 6. X-ray diffraction patterns of $x = 0.33$ annealed for 15 h at 140°C (a) and at 160°C (b). Open circles indicate the reflections of β-AgI, whereas the filled circles indicate the 1:1 phase (see Ref. (8)). Only the most intense reflections have been indicated.

The above findings are also supported by a more accurate analysis of the thermograms reported in Fig. 4. As stated in our previous work, this system presents an intermediate stable phase (1:1) which melts incongruently at ~250°C and a eutectic with $x \cong 0.25$ at ~180°C. The DSC thermogram of $x = 0.50$ sample (curve a) exhibits two small endothermic effects at temperatures below the melting peak at 250°C. The first one is surely associated with the $\beta \rightarrow \alpha$ transition of AgI, whereas the second is likely related to the eutectic between pure α-AgI and the 2:1 phase. These further two peaks should not be expected for pure $x = 0.50$ compound and are likely due to the devitrification of a small amount of glassy phase not completely removed by the annealing procedure. As expected, these residues of devitrification are hardly detectable in the DSC thermogram of $x = 0.7$ sample (curve b).

The overall results here described allow us to sketch the metastable phase diagram of the AgI:Ag_2MoO_4 system, which is reported in Fig. 7. The insert represents the corresponding equilibrium diagram, which is very similar to that early reported in Ref. (8). Let us now concentrate our attention to the out-of-equilibrium part of the figure: here the dashed lines represent kinetically controlled phase transitions, whereas the circles indicate the T_g's. The glass-forming region extends up to 70°C for $0.2 < x < 0.33$, whereas the upper limit of 110°C is reached only for $0.33 \le x < 0.4$. The dotted line at 70°C represents further nucleation of β-AgI in a composition range where crystalline β-AgI is already present in the as-quenched samples. At 175°C an eutectic between α-AgI and the 2:1 metastable compound is formed around $x = 0.25$, i.e. nearly at the same composition where the equilibrium phase diagram exhibits an eutectic between α-AgI and the 1:1 compound (see insert).

As already stated, a glassy phase is formed over the whole composition range which transforms into the 2:1 crystalline compound at ~110°C. The kinetically limited decomposition of this metastable compound becomes much faster when temperatures around ~180°C are attained. In fact, sample $x = 0.33$ shows partial decomposition into AgI and the 1:1 compound after 15 h of annealing at 160°C (see Fig. 6), whereas at 180°C the transformation takes place in the time scale of the DSC scan (~1 min), as shown in Fig. 1a.

The existence of a metastable crystalline compound near the eutectic is an impressive confirmation of the Angell's concept of the "barely stable crystal" (13), that suggests how two non-glass-forming compounds under certain conditions of nonideal mixing may produce glasses rather than crystals. Following Angell's idea, the most favorable situation for formation of glasses when cooling binary solutions will be

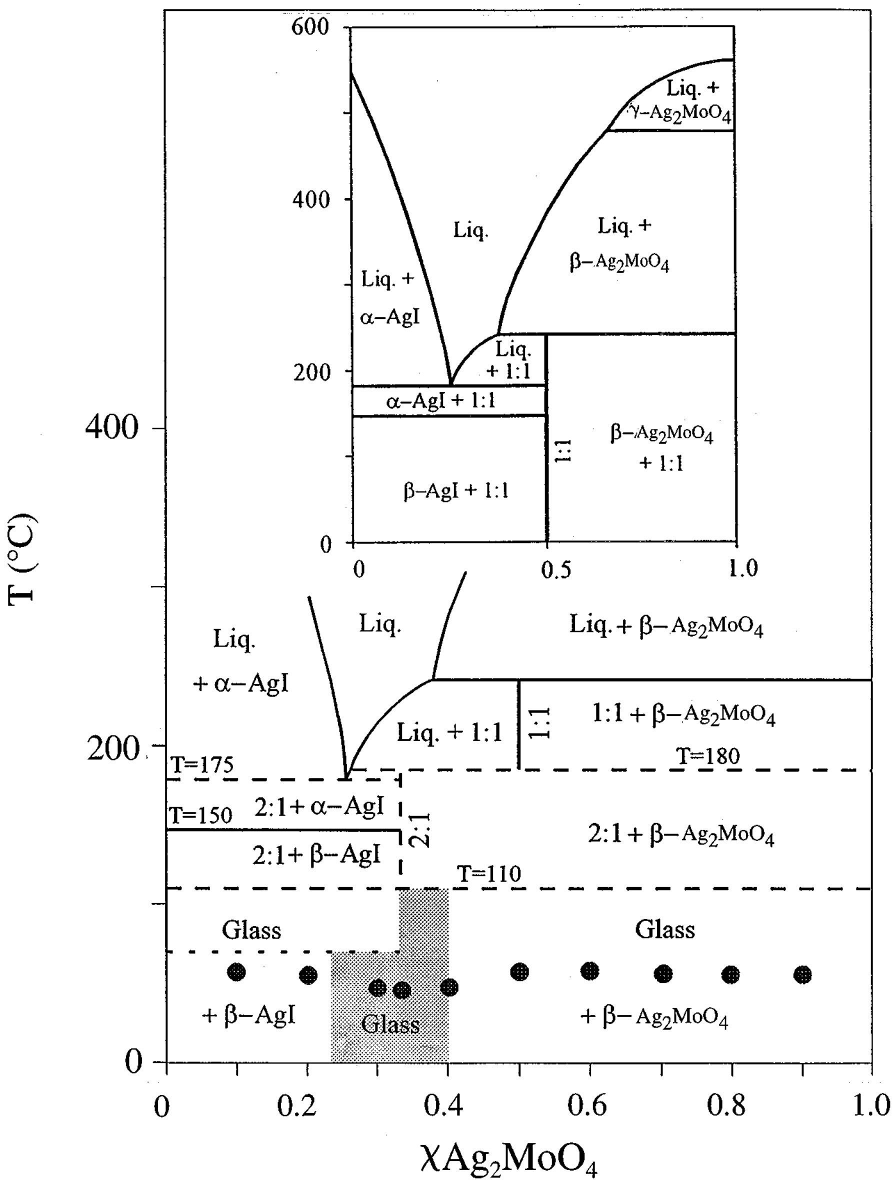

FIG. 7. Phase diagram of AgI : Ag_2MoO_4 system. The inset represents the equilibrium part. The shaded area indicates the glass formation region. The dashed lines give metastable phases boundaries. See text for the other symbols.

the intermediate case where the solvent–solute interactions are strong enough to depress the liquidus (the eutectic) much more than the ideal solutions but not strong enough to generate a crystalline compound with high lattice stability. The optimum situation for glass formation will be the one in which the exothermic mixing is strong enough to produce a single compound with poor structure. This is indeed the case of the 2:1 metastable compound we find near the eutectic. However, it is quite curious that a crystal with a relatively low lattice energy appears all over the composition range (see Fig. 4), well outside the glass formation region. On the other hand, the formation of a 2:1 compound seems to be common result in silver oxide systems (8, 14). Further investigations are in progress to clarify this point.

5. CONCLUSIONS

We have studied by DSC and XRD both kinetically limited and thermodynamic transformations of the system AgI : Ag_2MoO_4. The thermal effects not completely understood in Ref. (8) have now been addressed. We confirm that the glass-forming region spans over the range $0.20 < x < 0.40$ (4).

While we substantially confirm the equilibrium results we reported in (8), some interesting novelties are found chiefly in the AgI-rich part of the phase diagram:

(i) A metastable crystalline compound with composition $2AgI:Ag_2MoO_4$ nucleates at $\sim 110°C$ over the entire composition range. The stability of this phase is strongly temperature controlled: at $\sim 180°C$ it decomposes into AgI and 1 : 1 stable compound in a matter of 1 min.

(ii) Annealing the glass (or glass-ceramic) samples in the region $0 \leq x < 0.33$ near 70°C causes all AgI in excess of the 2 : 1 compound to crystallize as β phase.

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