



XANES and EXAFS at Mo K-edge in $(\text{AgI})_{1-x}(\text{Ag}_2\text{MoO}_4)_x$ glasses and crystals

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Abstract

$(\text{AgI})_{1-x}(\text{Ag}_2\text{MoO}_4)_x$ glasses and crystals have been studied by X-ray absorption spectroscopy at the Mo K-edge. All the measured samples contain isolated $[\text{MoO}_4]$ tetrahedra with $R(\text{Mo}-\text{O}) = 1.785 \pm 0.008 \text{ \AA}$ and mean square relative displacement (MSRD) $\sigma^2 = 0.0043 \pm 0.0013 \text{ \AA}^2$, which are unchanged upon insertion of AgI. The glasses have a quite similar environment around molybdenum, which resembles that of the crystal $(\text{AgI})_x(\text{Ag}_2\text{MoO}_4)_x$ with $x = 0.33$. The presence of AgI modifies the local environment around molybdenum already in the second coordination shell. © 1999 Published by Elsevier Science B.V. All rights reserved.

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1. Introduction

The pseudobinary glasses with composition $(\text{AgI})_{1-x}(\text{Ag}_2\text{MoO}_4)_x$ belong to fast ion conducting (FIC) glasses which can be used as electrolytes in solid state electrochemical devices like batteries and sensors. Such an application is favoured by the high values (of the order of $10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$) of conductivity displayed by silver-based glasses at room temperature.

The $(\text{AgI})_{1-x}(\text{Ag}_2\text{MoO}_4)_x$ glasses can be prepared in the range $0.2 < x \leq 0.4$. Their structural, transport and thermal properties were early studied by Minami

et al. [1,2], while the equilibrium phase diagram over the whole composition range was determined by our group [3]. The eutectic was found at $T \cong 180^\circ\text{C}$ for $x \cong 0.25$, whereas a peritectic was observed at 240°C , for $x \cong 0.5$ which corresponds to the formation of $(\text{AgI})_{0.5}(\text{Ag}_2\text{MoO}_4)_{0.5}$ (1:1 composition) compound.

We have recently revisited by DSC and X-ray diffraction the devitrification and the approach towards stability [4]: a metastable crystalline compound with composition $(\text{AgI})_{0.67}(\text{Ag}_2\text{MoO}_4)_{0.33}$ nucleates at $\sim 110^\circ\text{C}$ over the entire composition range.

In the present work, we present an X-ray absorption spectroscopy study of the local environment modifications around molybdenum ions in the

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AgI:Ag₂MoO₄ glass system upon composition change and thermal annealing.

2. Experimental

The following samples were used for X-ray measurements: crystalline c-Ag₂MoO₄, c-(AgI)_{0.5}(Ag₂MoO₄)_{0.5} ([1:1] composition) and c-(AgI)_{0.67}(Ag₂MoO₄)_{0.33} ([2:1] composition); glasses gl-(AgI)_{0.67}(Ag₂MoO₄)_{0.33} ([2:1] composition) and gl-(AgI)_{0.75}(Ag₂MoO₄)_{0.25} ([3:1] composition).

Glassy samples of the (AgI)_x(Ag₂MoO₄)_x system with $x = 0.25$ and $x = 0.25$ and $x = 0.33$ were prepared by the conventional melt-quenching technique. Appropriate mixtures of AgI and Ag₂MoO₄ (prepared by precipitation from aqueous solution of AgNO₃ and Na₂MoO₄ [5]), were melted at 600°C for 2 h in quartz tubes and then quenched to room temperature (RT) in stainless steel moulds. The [2:1] crystal has been obtained by heating the as-quenched sample $x = 0.33$ at 140°C for three days. The [1:1] crystal has been obtained by heating the as-quenched sample $x = 0.5$ at 160°C for three days.

X-ray absorption spectra were recorded at the Mo

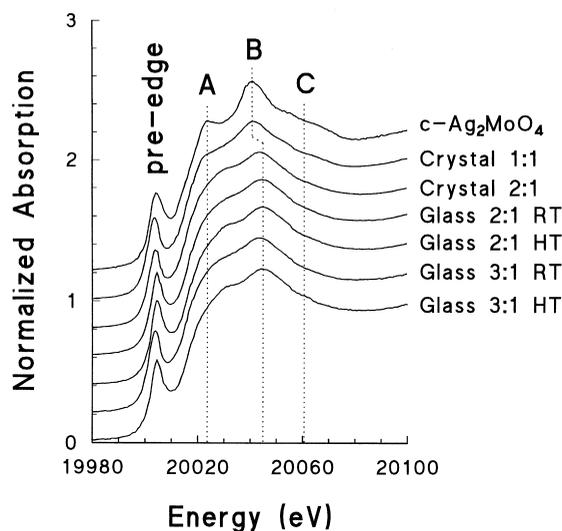


Fig. 1. Normalized Mo K-edge XANES spectra of c-Ag₂MoO₄, c-(AgI)_{0.5}(Ag₂MoO₄)_{0.5} (crystal 1:1), c-(AgI)_{0.67}(Ag₂MoO₄)_{0.33} (crystal 2:1), gl-(AgI)_{0.67}(Ag₂MoO₄)_{0.33} (glass 2:1) and gl-(AgI)_{0.75}(Ag₂MoO₄)_{0.25} (glass 3:1). For glasses, both room and high temperature (130°C, HT) data are shown.

K-edge in transmission mode at the ESRF (Grenoble, France) storage ring on the BM8 beamline:Italian CRG GILDA. The spectra for mixed crystals were recorded at RT and -93°C , whereas for glasses in the range from RT to 130°C to follow the crystallisation processes taking place in the range 70–120°C. The normalised X-ray absorption near edge structures (XANES) are shown in Fig. 1.

3. XAFS data analysis

The X-ray absorption spectra were analysed by the EDA software package [6,7]. A standard procedure [8,9] was applied to extract the extended X-ray absorption fine structure (EXAFS) signals. The Fourier transforms of some experimental EXAFS signals are shown in Fig. 2: they are all similar in the region of the first peak corresponding to four oxygen atoms of the first shell.

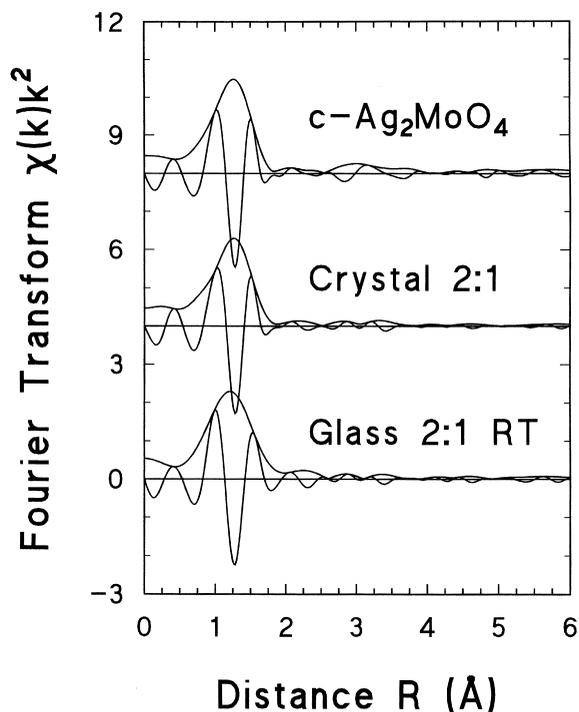


Fig. 2. Fourier transforms (FT) of the EXAFS $\chi(k)k^2$ signals for c-Ag₂MoO₄, c-(AgI)_{0.67}(Ag₂MoO₄)_{0.33} (crystal 2:1) and gl-(AgI)_{0.67}(Ag₂MoO₄)_{0.33} (glass 2:1). Both modulus and imaginary parts of FT are shown.

The first shell EXAFS contributions, corresponding to the nearest oxygen atoms, were singled out by the Fourier filtering; they were best-fitted in k -space using conventional single-shell Gaussian approximation and the model-independent method [6] which allows the radial distribution function (RDF) in case of arbitrary disorder to be reconstructed [10,11]. Both approaches gave similar results. A set of structural parameters were derived from the RDFs: the coordination number N , the interatomic distance R and the mean square relative displacement (MSRD), known as the EXAFS Debye–Waller factor σ^2 . The backscattering amplitude and phase shift functions, required in the calculation of the EXAFS signals, were obtained from cluster calculations for Ag_2MoO_4 performed by the ab initio FEFF6 code [12]. The structure of Ag_2MoO_4 was calculated from structural parameters given in Ref. [13].

The FEFF6 code was also used in the multiple-scattering (MS) calculations with the aim of interpreting the variation of the XANES signals.

4. Results and discussion

The comparison of the XANES signals (Fig. 1) allows the conclusion that only small changes occur in the molybdenum environment upon mixing with AgI and heat treatment. It is also shown that both glasses are more similar to the [2:1] crystal than to pure Ag_2MoO_4 or to the [1:1] crystal. The Mo K-edge XANES spectra for all compounds show a pre-edge peak of relatively high intensity, attributed to the $1s(\text{Mo}) \rightarrow 4d(\text{Mo}) + 2p(\text{O})$ transition, which is dipole-allowed for tetrahedral symmetry [10,11]. Note that for distorted octahedral coordination (e.g. in $\alpha\text{-MoO}_3$), the same transition results in a shoulder whereas for regular octahedron (e.g. in MoO_2), it is very weak and becomes nearly invisible at the Mo K-edge having large natural broadening [10,11].

Our calculations simulate the fine structure located above the E_0 point, which is located above the pre-edge peak. In pure c- Ag_2MoO_4 , the XANES signal, calculated for a cluster of 6 Å radius having Ag_2MoO_4 structure, is mainly determined by the following three contributions: (1) the full multiple-scattering (MS) within the first shell tetrahedron

$[\text{MoO}_4]$, (2) the single-scattering (SS) from 12 oxygens (O_2) in the second shell and (3) the double-scattering (DS) within the chains $\text{Mo}_0 \rightarrow \text{O}_1 \rightarrow \text{Ag}_3 \rightarrow \text{Mo}_0$ with the angle $\text{Mo}_0\text{O}_1\text{Ag}_3 \sim 130^\circ$ (24 paths totally). The latter two contributions are responsible in part for the shoulder A located at 20023 eV.

In the mixed $(\text{AgI})_{1-x}(\text{Ag}_2\text{MoO}_4)_x$ crystals and glasses the introduction of the iodine ions leads to a modification of the local environment around molybdenum already within the next neighbour shells. The main observed effect can be attributed to an expansion of the next-nearest distances around the Mo atoms, due to the large difference in the ionic radii of oxygen (1.32 Å) and iodine (2.20 Å) ions. Upon mixing Ag_2MoO_4 with AgI, the first shell around molybdenum remains unchanged, while the atoms composing the outer shells move aside so that the distances between them and the central Mo ion increase. Such an expansion results in the drastic decrease of the contributions from the outer shell atoms into the XANES so that it can be adequately described by considering only the MS effects within the first shell MoO_4 tetrahedron, which are more important in the XANES region (up to 200 eV above the edge) than in the EXAFS one.

Only small differences are induced by temperature in the XANES spectra of the measured glasses, resulting in slightly more structured spectra in the positions of the main features of the [2:1] crystal $(\text{AgI})_{0.67}(\text{Ag}_2\text{MoO}_4)_{0.33}$.

The first shell around molybdenum in all the compounds is composed of 4.0 ± 0.5 oxygen atoms forming a rigid tetrahedron with $R(\text{Mo}-\text{O}) = 1.785 \pm 0.008$ Å and MSRD $\sigma^2 = 0.0043 \pm 0.0013$ Å². Within our error bar, we cannot find any difference between crystals and glasses. However, within the precision of our experiment, we can exclude the presence of the six-fold coordinated molybdenum ions in our crystals and glasses. This conclusion is strongly supported by the following two results. First, the obtained structural parameters (N and R) correspond well to the ones usually found for the four-fold coordinated molybdenum ions [13]. Second, in the case of the six-fold coordination, one expects to have a strongly distorted octahedron for Mo(VI) ($4d^0$ -configuration) ions due to the second-order Jahn–Teller effect. Such a distortion, consist-

ing of a large splitting of the Mo–O distance distribution into two or three sub-shells, which can be clearly observed from the EXAFS analysis [10,11], is not present in the case of the measured $(\text{AgI})_{1-x}(\text{Ag}_2\text{MoO}_4)_x$ compounds.

5. Conclusions

The local environment around molybdenum ions has been studied by X-ray absorption spectroscopy at the Mo K-edge in crystalline pure $\text{c-Ag}_2\text{MoO}_4$; mixed crystals $\text{c-(AgI)}_x(\text{Ag}_2\text{MoO}_4)_x$ with $x = 0.50$ (1:1) and 0.33 (2:1); mixed glasses $\text{gl-(AgI)}_{1-x}(\text{Ag}_2\text{MoO}_4)_x$ with $x = 0.33$ (2:1) and 0.25 (3:1). The spectra for mixed crystals were recorded at RT and -93°C , whereas for mixed glasses in the range from RT to 130°C to follow the partial crystallisation at 100°C .

All the measured samples contain isolated $[\text{MoO}_4]$ tetrahedra with $R(\text{Mo-O}) = 1.785 \pm 0.008 \text{ \AA}$ and MSRD $\sigma^2 = 0.0043 \pm 0.0013 \text{ \AA}^2$, which are unchanged upon insertion of AgI.

The measured glasses have a quite similar environment around molybdenum in the outer shells, which resembles that of the [2:1] crystal $(\text{AgI})_{1-x}(\text{Ag}_2\text{MoO}_4)_x$ ($x = 0.33$). The presence of AgI modifies the coordination of Mo already in the second shell.

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