

Correlation Between I-Ag Distance and Ionic Conductivity in AgI Fast-Ion-Conducting Glasses

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A large number of AgI-based fast-ion-conducting glasses have been investigated by K-iodine extended x-ray absorption fine structure spectroscopy (EXAFS) measurements at liquid nitrogen temperature. A general correlation between the I-Ag distance measured by EXAFS and the glass activation energy for dc ionic conductivity has been found out: glasses with longer I-Ag distances display higher ionic conductivity, independently from the chemical composition of their host glassy matrix. This behavior can be related to the progressive increase of the “pathway volume” for ionic conduction.

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Fast-ion-conducting (FIC) glasses, whose values of ionic conductivity are comparable to those of liquid electrolytes, are of wide interest for their potential applications in solid electrochemical devices, including batteries, sensors, and smart windows. The understanding of transport properties in FIC glasses is a challenging problem both from applied and basic research point of view, whose knowledge may allow us to design new glasses with optimized properties for various applications. Although many experimental and theoretical efforts have led to some general rules and empirical relations for high ionic conductivity, there is not yet any satisfactory and widely accepted transport model [1–4].

It is well known that the ionic conductivity increases drastically when a modified glass is doped by a metal-halide salt [5]. Using conductivity and density data for various oxide glasses mixed with various metal-halide salts, a general relation between conductivity enhancement and expansion of the host glassy matrix, induced by the salt doping, has been observed by Swenson and Börjesson [6]. In the same work, the authors suggest that the expansion of the host glassy matrix is a key parameter determining the increase of the ionic conductivity, and it is related to the available “free volume” for ions transport.

Among FIC glasses, AgI-doped glasses are the best conducting oxide glasses, with room-temperature conductivities up to nearly $10^{-1} \Omega^{-1} \text{cm}^{-1}$. Applying a bond-valence method to reverse Monte Carlo produced structural models of AgI-based superionic glasses, Adams and Swenson determined both ionic conductivity and activation energy from the so-called pathway volume, that is the available volume for ionic transport in which the majority of the Ag ions that contribute to the conductivity has a mixed oxide-iodide coordination [7,8]. In these works, the authors preferred the term pathway volume to the term free volume in order to underline that the effect of the free

volume is not independent of its spatial distribution and of the surrounding anions.

Although the influence of the AgI dopant salt on the glass structure and ionic conductivity has been widely investigated, leading to some commonly accepted ideas [4], a full connection between local structure and ionic conductivity is still lacking. To this aim, extended x-ray absorption fine structure spectroscopy (EXAFS) is particularly suited to study the local environment of a given x-ray absorbing atom, thanks to selectivity of atomic species, and high sensitivity to short-range order. Recent EXAFS measurements on AgI-glasses, as a function of temperature, have given new information on the local modifications around iodine due to increase with temperature of the ionic diffusivity [9,10].

This Letter reports an EXAFS investigation of the local structure around Iodine in different families of AgI-based glasses (borates, phosphates, molybdates, tungstates) as a function of their ionic conductivity. From a phenomenological point of view, the dc ionic conductivity σ is described by Arrhenius law $\sigma T = A \exp(-E_a/k_B T)$, where the activation energy E_a is the mean energy for a “cation jump” [11]. At constant temperature, $\log(\sigma)$ linearly increases with the decrease of E_a . In this work we have found out, for the first time, a general correlation between the I-Ag distance measured by EXAFS and the glass activation energy E_a for ionic conductivity.

EXAFS measurements at liquid nitrogen (LN) temperature were performed at the *K* edge of Iodine at the BM29 beam line of ESRF (European Synchrotron Radiation Facility), Grenoble, on the families of AgI-based glasses listed in Table I. Besides their different chemical composition, these glasses display structural difference on their host matrices: in silver borate and silver phosphate glasses, the host glass matrix ($\text{Ag}_2\text{O-B}_2\text{O}_3$ and AgPO_3 , respectively) forms a continuous random network, while silver

TABLE I. List of AgI-glasses investigated in this work and corresponding activation energy for dc ionic conductivity, by references in square brackets.

Glass	Activation energy, E_a (eV)
(AgI) _{0.60} (Ag ₂ O : 1 · B ₂ O ₃) _{0.40}	0.28 [11]
(AgI) _{0.70} (Ag ₂ O : 1 · B ₂ O ₃) _{0.30}	0.23 [11]
(AgI) _{0.75} (Ag ₂ O : 1 · B ₂ O ₃) _{0.25}	0.22 [11]
(AgI) _{0.10} (Ag ₂ O : 2 · B ₂ O ₃) _{0.90}	0.48 [11]
(AgI) _{0.20} (Ag ₂ O : 2 · B ₂ O ₃) _{0.80}	0.44 [11]
(AgI) _{0.30} (Ag ₂ O : 2 · B ₂ O ₃) _{0.70}	0.38 [11]
(AgI) _{0.40} (Ag ₂ O : 2 · B ₂ O ₃) _{0.60}	0.35 [11]
(AgI) _{0.50} (Ag ₂ O : 2 · B ₂ O ₃) _{0.50}	0.31 [11]
(AgI) _{0.60} (Ag ₂ O : 2 · B ₂ O ₃) _{0.40}	0.27 [11]
(AgI) _{0.20} (Ag ₂ O : 3 · B ₂ O ₃) _{0.80}	0.54 [11]
(AgI) _{0.40} (Ag ₂ O : 3 · B ₂ O ₃) _{0.60}	0.42 [11]
(AgI) _{0.10} (Ag ₂ O : 4 · B ₂ O ₃) _{0.90}	0.74 [11]
(AgI) _{0.20} (Ag ₂ O : 4 · B ₂ O ₃) _{0.80}	0.65 [11]
(AgI) _{0.30} (Ag ₂ O : 4 · B ₂ O ₃) _{0.70}	0.57 [11]
(AgI) _{0.40} (Ag ₂ O : 4 · B ₂ O ₃) _{0.60}	0.47 [11]
(AgI) _{0.50} (Ag ₂ O : 4 · B ₂ O ₃) _{0.50}	0.39 [11]
(AgI) _{0.55} (Ag ₂ O : 4 · B ₂ O ₃) _{0.45}	0.35 [11]
(AgI) _{0.30} (AgPO ₃) _{0.70}	0.36 [12,13]
(AgI) _{0.50} (AgPO ₃) _{0.50}	0.26 [12,13]
(AgI) _{0.67} (Ag ₂ MoO ₄) _{0.33}	0.24 [14,15]
(AgI) _{0.75} (Ag ₂ MoO ₄) _{0.25}	0.20 [14,15]
(AgI) _{0.65} (Ag ₂ WO ₄) _{0.35}	0.23 [16]
(AgI) _{0.70} (Ag ₂ WO ₄) _{0.30}	0.21 [16]
(AgI) _{0.75} (Ag ₂ WO ₄) _{0.25}	0.19 [16]

molybdate (or tungstate) glasses are depolymerized systems where the oxyanions, generally MoO₄²⁻ tetrahedra, do not form networks. The glasses were prepared by melt-quenching technique, following the procedure reported in Ref. [11] for borate glasses, Ref. [12] for phosphate glasses, Ref. [15] for molybdate glasses, and Ref. [16] for tungstate glasses. The possible presence of significant crystallites in the glasses was ruled out by the absence of any detectable Bragg peaks in x-ray diffraction patterns.

The EXAFS measurements were done in transmission mode, with x-ray beam monochromatized by two parallel silicon crystals with flat reflecting (311) faces, detuned to reduce the harmonics influence. To get homogeneous samples of uniform thickness, the glasses were powdered, dispersed in alcohol and slowly deposited on polytetrafluoroethylene membranes. The thickness being chosen so as to have, when possible, an absorption edge jump $\Delta\mu x \approx 1$. Crystalline β -AgI was also measured as reference.

The edges of all collected spectra were aligned to within 0.1 eV or better, in order to obtain a resolution of the order of 0.001 Å in relative distances. The EXAFS signals $\chi(k)$, where k is the photoelectron wave vector, were extracted from the experimental spectra according to well established procedures [17], and display a good quality up to 15 Å⁻¹ (top panels in Fig. 1). The $k\chi(k)$ weighted EXAFS

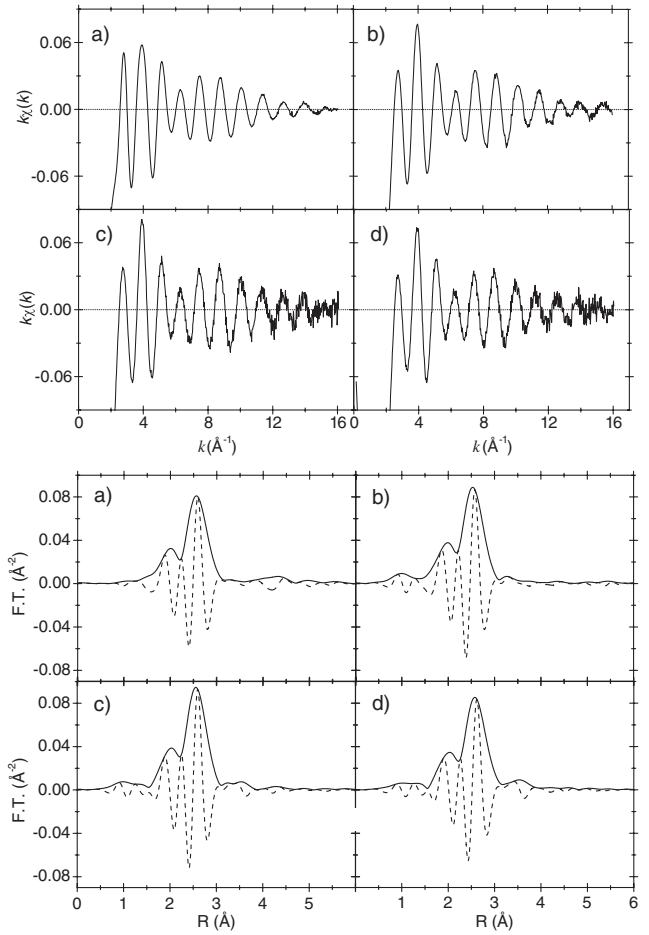


FIG. 1. EXAFS signals $k\chi(k)$ (top panels) and corresponding Fourier transforms (bottom panels) in crystalline β -AgI at 300 K (panels a) and in three selected glasses at LN temperature: (AgI)_{0.50}(Ag₂O : 4 · B₂O₃)_{0.50} (panels b), (AgI)_{0.50}(AgPO₃)_{0.50} (panels c), (AgI)_{0.70}(Ag₂WO₄)_{0.30} (panels d). Dashed and continuous lines in the Fourier transform are the imaginary part and the modulus, respectively.

signals were Fourier transformed in the interval $k = 2.5\text{--}14 \text{ \AA}^{-1}$ using a Gaussian window. The Fourier transforms of the EXAFS signals of selected glasses and crystalline β -AgI are compared in the bottom panels of Fig. 1. All glasses display a striking similarity in the Fourier transform. Like β -AgI, the structure between about 1.5 and 3 Å is due to the contribution of nearest neighbors Ag ions (the double peak is due to the shape of the backscattering amplitude of silver). A nearest-neighbor link between negative iodine and oxygen ions is highly improbable. No neat contribution from farther neighbors is visible, owing to the effect of disorder.

The structure between about 1.5 and 3 Å was Fourier back-transformed, and the filtered EXAFS signal analyzed by the ratio method through the cumulant approach [17–19], using crystalline β -AgI at LN temperature as reference for backscattering amplitudes, phase shifts, and in-

elastic terms. The cumulant analysis allows one to determine the main parameters which describe the distance distribution between the EXAFS absorbing atom and its nearest-neighbors, as mean distance, variance, skew parameter and coordination number. Following the pioneering studies of Boyce *et al.* [20,21] on the superionic phase transition of AgI, the EXAFS cumulants obtained from the ratio method, instead of being referred to the whole distribution of nearest-neighbor silver ions, are considered to parameterize only the short-range component of the whole I-Ag distribution; the remaining long-range component, which escapes EXAFS detection, contains Ag ions undergoing diffusion and highly disordered. This interpretation of EXAFS cumulants has been successfully tested in a recent EXAFS study on silver molybdate glasses as a function of temperature, by means of a Monte Carlo procedure [9].

Figure 2 shows, for each glass listed in Table I, the I-Ag distance obtained from our EXAFS measurements, plotted against the corresponding activation energy for dc ionic conductivity. The absolute value has been determined by comparison with crystalline β -AgI at LN temperature, where the I-Ag distance has been assumed to be 2.80 Å (the exact value is unimportant). The other parameters describing the I-Ag distance distribution (less important for the aim of this work), i.e., variance (C_2^*), skew parameter ($C_3^*/C_2^{*1.5}$) and coordination number, are within the range of about 0.011–0.014 Å², 0.4–0.6, and 3.3–3.9, respectively. Also in this case, the absolute values have been determined by comparison with crystalline β -AgI at LN

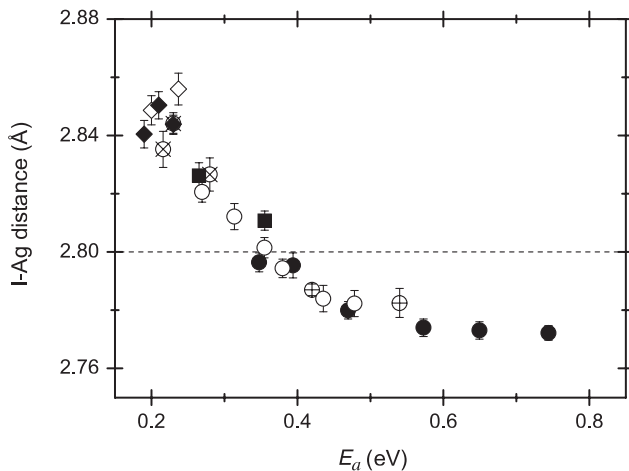


FIG. 2. Mean I-Ag distance measured by EXAFS in different families of AgI-based glasses at LN temperature, plotted against their activation energy for dc ionic conductivity. The symbols refer to the glass family: \otimes = AgI-Ag₂O-1 · B₂O₃, \circ = AgI-Ag₂O-2 · B₂O₃, \oplus = AgI-Ag₂O-3 · B₂O₃, \bullet = AgI-Ag₂O-4 · B₂O₃, \blacksquare = AgI-AgPO₃, \blacklozenge = AgI-Ag₂MoO₄, \blacklozenge = AgI-Ag₂WO₄. Dashed line is the reference value of crystalline β -AgI at LN temperature.

temperature, where $C_2^* \approx 0.0043$ Å², $C_3^*/C_2^{*1.5} \approx 0.18$, and the coordination number is 4.

The most striking result of this work is the detection of a general correlation between the I-Ag distance measured by EXAFS and the glass activation energy for ionic conductivity (Fig. 2). The I-Ag distance progressively increases from 2.77 Å in glasses with low ionic conductivity (i.e. high activation energy and low content of AgI), to about 2.85 Å in glasses with high ionic conductivity (i.e. low activation energy and high content of AgI). In particular, glasses with activation energy lower than about 0.35 eV display longer I-Ag distances than in crystalline β -AgI, and viceversa. As a result, the I-Ag distance plays a key role on the conductivity enhancement of AgI FIC glasses, independently from the chemical composition of the host glassy matrix.

We can guess a connection between the progressive expansion of the I-Ag distance and the progressive increase of the pathway volume for ionic conduction defined by Adams and Swenson. To this aim, let us consider the works of these authors, in which a “linear relationship” between activation energy and “cube root” of the pathway volume was determined [7,8]. For each glass listed in Table I, we have calculated the mean volume of the I-Ag coordination sphere as $V = \frac{4}{3}\pi C_1^{*3}$, where C_1^* is the corresponding I-Ag distance reported in Fig. 2. Indicating with V_0 the volume sphere of the glass with the shortest I-Ag distance [i.e., the borate glass (AgI)_{0.10}(Ag₂O-4B₂O₃)_{0.90}] we have calculated the quantity $\sqrt[3]{V - V_0}$, which represents the cube root of the volume expansion between Ag and I ions. As shown in Fig. 3, it can be observed a linear relationship between the quantity $\sqrt[3]{V - V_0}$ and the activation energy for dc ionic conductivity. Accordingly, by comparison with Adams and Swenson works, $V - V_0$ shows an analogous behavior to that displayed by the pathway volume. As a

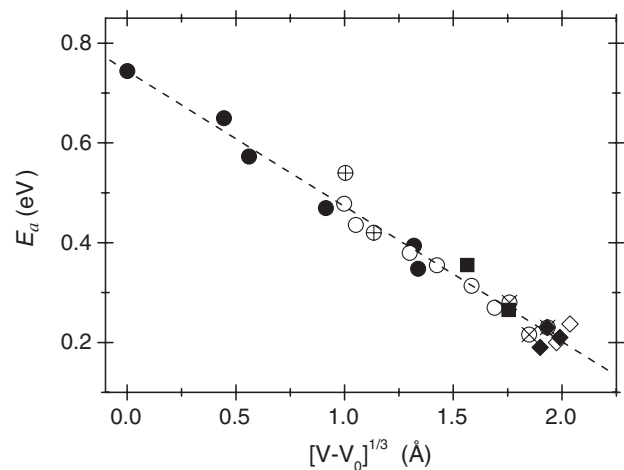


FIG. 3. The linear relationship between activation energy for dc ionic conductivity and cube root of the volume expansion $V - V_0$ between Ag and I ions. Symbols are the same as in Fig. 2.

consequence, although $V - V_0$ cannot be identified as the pathway volume, it can be assumed that the I-Ag expansion is connected to the increase of the pathway volume. In agreement with recent models, according to which the pathways for ionic conduction are characterized by mixed iodine and oxygen environments [4,8], the expansion of the I-Ag distance could be attributed to the progressive growth of Ag ions with mixed oxygen and iodine coordination, in which oxygens attract Ag ions expanding the mean I-Ag distance.

Before concluding, let us make a last consideration on the activation energy. It is well known that the activation energy can be written as a sum of two terms: the first is denoted binding energy and is the mean energy a cation requires to leave its site, the second is denoted strain energy and is the mean kinetic energy a cation needs to open a “doorway” in the structure to pass through. The decrease of the activation energy induced by salt doping was mainly associated to a lowering of the strain energy [7]. However, on the basis of the present experimental results (i.e., decrease of the activation energy with increase of the I-Ag distance), we can guess that also the binding energy term gives a significant contribution on the enhancement of ionic conduction.

In conclusion, in this work a general correlation between ionic conductivity and I-Ag distance has been found out in AgI-based FIC glasses. Glasses with longer I-Ag distances display higher ionic conductivity, independently from the chemical composition of their host glassy matrix. Finally, the I-Ag expansion has been related to the progressive increase of the pathway volume for ionic conduction, in which the mean I-Ag distance could be expanded by the progressive growth of Ag ions with mixed I/O coordination.

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