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Long-range structural correlations in amorphous ternary In-based oxides

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ABSTRACT

Systematic investigations of ternary In-based amorphous oxides, In–X–O with X = Sn, Zn, Ga, Cd, Ge, Sc, Y, or La, are performed using ab-initio molecular-dynamics liquid-quench simulations. The results reveal that the local M–O structure remains nearly intact upon crystalline to amorphous transition and exhibit weak dependence on the composition. In marked contrast, the structural characteristics of the metal–metal shell, namely, the M–M distances and M–O–M angles that determine how MO polyhedra are connected into a network, are affected by the presence of X. Complex interplay between several factors such as the cation ionic size, metal–oxygen bond strength, as well as the natural preference for edge, corner, or face-sharing between the MO polyhedra, leads to a correlated behavior in the long-range structure. These findings highlight the mechanisms of the amorphous structure formation as well as the specifics of the carrier transport in these oxides.

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1. Introduction

Although the unique properties of transparent amorphous oxide conducting and semiconducting materials were first demonstrated almost a decade ago [1,2], basic structural properties of these oxides – namely, the structural characteristics associated with the crystalline-to-amorphous transition – are far from understood. Most of the experimental characterization of the transparent amorphous oxides deal almost exclusively with the first shell, i.e., the coordination of oxygen atoms around metal cations [3–9]. Similarly, available theoretical models derived from molecular dynamics (MD) simulations of the amorphous oxides focus primarily on the Metal–Oxygen data with no or limited information on the Metal–Metal distances and coordination [10–18]. However, the first-shell remains nearly intact upon the crystalline-to-amorphous transition, owing to the strong oxygen electronegativity. Instead, integration of the Metal–Oxygen polyhedra into a continuous network – governed by the Metal–Metal distances, coordination, and oxygen sharing – plays a key role in the formation and properties of the amorphous oxides. Indeed, recent experimental and theoretical investigations of amorphous indium oxide [19] revealed that interconnectivity and spatial distribution of the InO polyhedra determines the electron transport limited by charge scattering: the observed peak in the electron mobility was found to correspond to the structure with long chains of InO_6 polyhedra connected primarily via corner sharing.

To gain a thorough systematic understanding of the role of composition in the structural properties of amorphous In-based oxides, eight ternary In–X–O structures with X = Sn, Zn, Ga, Cd, Ge, Sc, Y, or La, denoted below as a-IXO, were modeled using liquid-quench MD simulations. The choice for X cations in this study covers the typical compositional chemistry in both crystalline and amorphous transparent conducting and semiconducting oxides: all cations are pre- or post-transition metals with ns^0 electronic configuration. The structural characteristics of the first, second, and third shells as well as the connectivity between the MO polyhedra are compared for amorphous indium oxide (a-IO) and a-IXO. The results highlight the importance of the spatial distribution of the InO_6 and XO polyhedra from the point of view of amorphization and charge transport and facilitate the progress in fundamental understanding of amorphous oxides.

2. Computational method

The amorphous a-InO and a-InXO structures were generated using first-principles molecular dynamics as implemented in the Vienna Ab Initio Simulation package (VASP) [20–23]. The calculations are based on the density functional theory (DFT) [24,25] with

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PBE functional based on the projector augmented-wave method [26–28]. For the initial structure, we used a cubic 130-atom cell of bixbyite In_2O_3 with density 7.12 gm/cm^3. To obtain ternary IXO structures, we randomly replaced 20% of the In atoms in the initial structure by respective metal X (Sn, Zn, Ga, Cd, Ge, Sc, Y or La) and adjusted (i) the number of oxygen atoms to maintain stoichiometry; and (ii) the cell volume to maintain the density in the In-based samples. The resulting lattice parameters that we have used in our studies are: 11.898 Å for InO; 12.11 Å for InSnO; 11.78 Å for InZnO; 11.80 Å for InGaO; 12.06 Å for InCdO; 11.86 Å for InGeO; 11.66 Å for InScO; 11.91 Å for InYO; and 12.17 Å for InLaO.

For each initial IO or IXO structure, we performed molecular dynamics simulations of liquid quench as follows. First, to remove any crystalline memory, each initial structure was melted at 3000 K for 6 ps. The melt was then cooled to 1700 K at the rate of 100 K/1.2 ps, and then rapidly quenched to 100 K at the rate of 200 K/1.2 ps. In order to make the calculations computationally efficient, we used low cut-off of 260 eV and restricted the *k*-point sampling to Γ point only during melting and quenching processes. Finally, each structure was equilibrated at 300 K for 6 ps with a cut-off energy of 400 eV. All simulations were carried out within NVT ensemble with Nose'-Hoover thermostat using integration time step of 2 fs.

3. Results and discussion

3.1. In—O and X—O distances in amorphous IO and IXO

To understand the role of composition in the structural properties of amorphous In-based oxides, first, the local structure of the InO_x polyhedra in a-IO and a-IXO with X = Sn, Zn, Ga, Cd, Ge, Sc, Y, or La, is analyzed. For this, the distribution of the In—O distances and the In coordination with oxygen atoms in a-IXO are compared to the corresponding In—O values in a-IO as well as those in crystalline In_2O_3. For an accurate comparison of the average In—O distances in a-IO and a-IXO, the average pair correlation function [29,30] was calculated according to:

$$l_{av} = \frac{\sum_i l_i \exp\left(1-\left(\frac{l_i}{l_{\min}}\right)^6\right)}{\sum\limits_i \exp\left(1-\left(\frac{l_i}{l_{\min}}\right)^6\right)} \qquad (1)$$

where the summation runs over all oxygen neighbors of a particular In atom and $l_{\min}$ is the smallest In—O distance in the *i*-th InO_x polyhedron. The results, shown in Fig. 1, reveal that the average pair correlation function increases for X = Sn, Zn, Ga, or Ge, and decreases for X = Cd, Sc, La, or Y, with respect to the In—O value in a-IO. The average In—O distance in all In-based oxides remains to be below the corresponding value in crystalline In_2O_3, namely, 2.18 Å. The shortest average In—O distance in case of a-IYO is in accord with the short In—O distance in crystalline hexagonal $YInO_3$, namely, 2.10 Å.

The above trends in the average In—O distance in a-IXO, Fig. 1, reveal no correlation with the ionic radii of the X cations. Indeed, the In—O distance cannot be affected directly by the presence of X cation since the In—O—M bond angle (M = In or X) is significantly less than 180° (on average, the In—O—M angles are equal to 98° and 116° for edge- and corner-shared In—M pairs, respectively.) For all X, the changes in the average In—O correlation function are insignificant, i.e., less than 1%. Moreover, the presence of X appears to have little effect on the radial In—O distance distribution: the calculated standard deviation, σ^2, shows only a small variation with composition, Fig. 1. The standard deviation increases for X = Ga or Ge which may be explained by their small ionic radii and the strength of the X—O bonds. A different mechanism should be sought for X = Sn in order to explain the increase of the average In—O distance and the distance distribution in a-ITO with respect to a-IO, c.f., Fig. 1. We believe that spatial distribution and connectivity of SnO_x and InO_6 polyhedra in a-ITO are important in determining the structural characteristics, as described below.

It is important to stress that local changes in the InO structure averaged out by the standard characterization procedures, Fig. 1, may be important from the crystallization and charge transport points of view. In particular, the strength of the X—O bonds with respect to that of the In—O bond (the so-called “oxygen-getter” behavior of X cation [31]) may affect the local In—O structure: (i) by introducing a “ripple” effect when the In—O bond distance fluctuates with the number of X neighbors [32]; and (ii) by changing the relative contributions from the differently coordinated In atoms (discussed below). Clearly, the spatial distribution of XO polyhedra within the InO framework (e.g., clustering *vs* uniform distribution of XO) becomes critical in determining the crystalline to amorphous transition as well as the transport properties (conductivity paths and scattering) in multicomponent oxides and will be addressed below.

The calculated average pair correlation function l_{av}(X—O), Eq. (1), for each a-IXO structure is given in Fig. 2. The results reveal that for X = Sn, Cd, Ge, Sc, or Y (for X = Zn, Ga, or La), the average X—O distance is shorter (longer) than the natural X—O distance, i.e., the distance in the corresponding crystalline binary oxides. Interestingly, the X—O distances in the available crystalline ternary In-containing oxides (we considered $In_4Sn_3O_{12}$, In_2ZnO_4, $GaInO_3$,

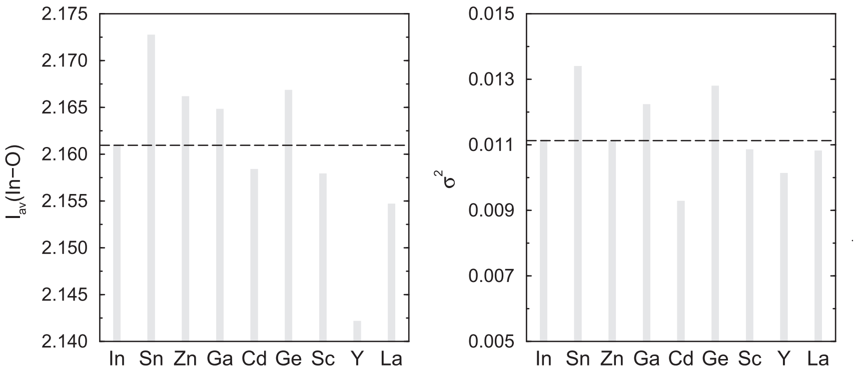

Fig. 1. (Left) Calculated average In—O pair correlation function, l_{av}, in Å, for amorphous IO and IXO. (Right) Calculated standard deviation of the radial In—O distance distribution, σ^2, in Å^2, for amorphous IO and IXO. The horizontal dash lines represent the corresponding values in amorphous IO.

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