



First principles study of the structural, electronic, and optical properties of Sn²⁺-doped ZnO–P₂O₅ glasses

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ABSTRACT

The atomic-structural, electronic, and optical properties of Sn-doped ZnO–P₂O₅ glasses are examined using combined semi-empirical and density functional theory calculations. From model structures for two different ZnO–P₂O₅ glass compositions, it is found that these glasses consist of nearly ideal tetrahedral PO₄ unit and largely distorted ZnO₄ and ZnO₅ units. The concentration of ZnO₅ units is calculated to increase and exceed that of ZnO₄ as the amount of ZnO in the glass is increased. Also, the concentration of terminal oxygen atoms shared by two Zn neighbors is largely increased for 70ZnO:30P₂O₅ (70:30) glass compared to 60:40 glass, which can be rationalized by electrostatic bond strength calculations. Regarding medium-range order, calculations show that Q₁ and Q₂ structures (where Q_n refers to structures containing *n* bridging oxygen atoms on PO₄ tetrahedra) are dominant for the 60:40 glass, while Q₀ and Q₁ prevail for the 70:30 glass, in good agreement with experimental observations. For the Sn-doped ZnO–P₂O₅ glass, various Sn coordination geometries are found, with trigonal pyramidal SnO₃ and largely distorted pyramidal SnO₄ configurations being dominant and a small fraction of two-fold and five-fold coordinated Sn configurations also present. From combined cluster and glass model calculations, two-fold coordinated Sn are found to exhibit slightly smaller optical transition energy than three-fold and four-fold coordinated Sn. However, local variations in coordination structures throughout the glass likely result in a broad singlet transition (S₀ → S₁) around 5.4 eV for all the different Sn configurations. A triplet transition (S₀ → T₁) driven by spin-orbit coupling can occur around 4.5–4.8 eV, but the magnitude of this transition is predicted to be much smaller than the spin-allowed singlet transition.

1. Introduction

Recently, Sn-doped ZnO–P₂O₅ glass has attracted considerable attention as a rare earth-free phosphor or scintillator material excited by UV, X-ray or γ -ray photons [1–9]. Being a post-transition metal, Sn²⁺ comprises a ns²-type emission center with *n* ≥ 4, where the electrons in the outermost shells (ns and np) are involved in the excitation and emission processes (ns² ⇒ ns¹np¹). As a result, local variations of the Sn²⁺ coordination environments in the glassy network can strongly affect the electronic and optical properties of Sn-doped ZnO–P₂O₅ glass, leading to broad excitation and emission lines [1–5,7–9]. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra of Sn-doped ZnO–P₂O₅ glass have shown two excitation peaks at around 5.3 and 4.4 eV, but only one emission peak at around 3.0 eV [3, 8, 9]. The intensity of the higher-energy excitation peak is found to be largely reduced compared to that of the lower-energy peak for higher SnO concentration (up to 5 mol%) or for higher ZnO composition in the host ZnO–P₂O₅ glass [3, 6–8]. It has been speculated that the two excitation

channels might be related to two different Sn coordination geometries (two-fold and four-fold coordinated) [5]. However, it is difficult to experimentally examine the relationship between the Sn coordination environments and their electronic and optical properties, due to existence of various Sn coordination geometries in the glass structure. Thus, theoretical calculations are necessary to examine the individual coordination environments and determine their associated properties.

In this work, we construct models for ZnO–P₂O₅ glasses with two different compositions (60ZnO:40P₂O₅ and 70ZnO:30P₂O₅, or “60:40” and “70:30”, respectively) using semi-empirical and density functional theory calculations. The structural parameters of our glass models at short-range and medium-range agree well with Nuclear Magnetic Resonance (NMR) and X-ray diffraction data [10–12]. For Sn-doped ZnO–P₂O₅ glasses, we examine the geometries of SnO configurations, which show various Sn coordination numbers from two to five. To simplify the interpretation of the relationship between the coordination environment and optical properties, we employ cluster model calculations for the two-fold, three-fold, and four-fold coordinated Sn–O_n

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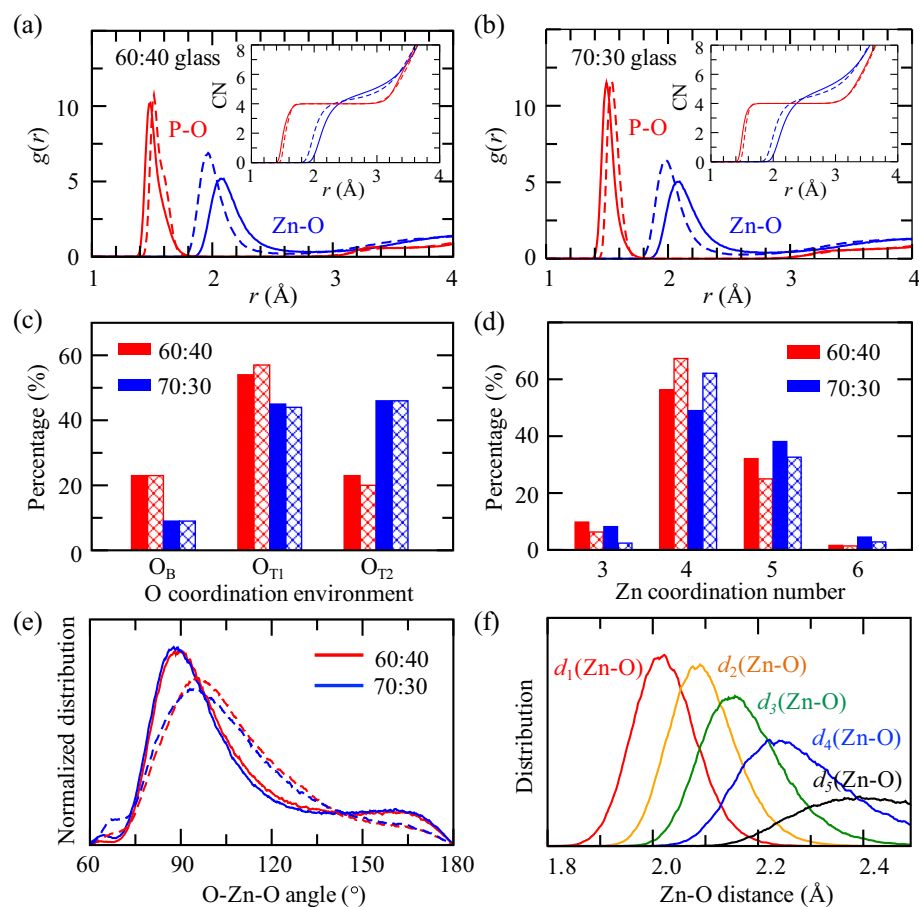


Fig. 1. Radial distribution function $g(r)$ for the P–O (in red) and Zn–O (in blue) pairs in (a) 60:40 and (b) 70:30 glass models. The insets of $g(r)$ plots show accumulated coordination number (CN) for P and Zn by O atoms. The solid and dotted lines represent structural parameters obtained from the classical MD and FPMD simulations, respectively. Distribution of (c) bridging (O_B) and terminal (O_{T1} and O_{T2}) oxygen concentrations and (d) Zn coordination number in 60:40 (in red) and 70:30 (in blue) glasses. Filled and hatched boxes indicate the classical MD and FPMD, respectively. For the analysis of Zn–O coordination environment, distribution of average O–Zn–O bond angle in 60:40 and 70:30 glasses [in (e)] and Zn–O bond distances in 70:30 glass [in (f)] are shown. In (e), the solid and dotted lines indicate the classical MD and FPMD, respectively. In (f), $d_n(\text{Zn–O})$ denotes the distance of Zn with n th O neighbor. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

configurations, and correlate to structures and electronic properties in the full glass models. Our calculations show that there is a dependency of electronic and optical properties on the coordination number, but it might be less significant than overall local structural variations in the glass for Sn dopants having the same coordination number.

2. Methods

Initial atomistic models of the 60:40 and 70:30 ZnO–P₂O₅ glasses are obtained using classical molecular dynamics (MD) melt-quench simulations, carried out using the LAMMPS package [13]. The potential employed is from [14] and consists of two-body (P–O, O–O, and Zn–O) and three-body (O–P–O and P–O–P) terms. The models for the 60:40 glass structures contained 36 ZnO and 24 P₂O₅ formula units in the simulation cell, while those for 70:30 glass had 42 ZnO and 18 P₂O₅ formula units. The initial volume was determined from the experimental densities of 3.442 and 3.779 g/cm³, respectively, for the 60:40 and 70:30 glass [10]. Before starting the melt-quench process, the initial structures were equilibrated for 100 ps at 300 K; then, the temperature was increased from 300 K to 3000 K over 500 ps while gradually increasing the volume by 15% to include thermal expansion effects [15, 16]. The melt was held at 3000 K for 500 ps and then at 2000 K for an additional 500 ps. After that, 10 snapshots were taken every 50 ps from further dynamics at 2000 K to obtain a large statistical distribution of local and independent glass structures. The final structures were obtained by taking each melted snapshot and quenching to 300 K with a quench rate of 10¹¹ K/s [17]. During quenching, the volume is reduced back to the initial pre-melted volume to account for thermal contractions. Finally, the quenched structures were equilibrated at 300 K and 1 atm for 2 ns under constant pressure and temperature (NPT) conditions to ensure that the structure is fully optimized

under ambient pressure. For all classical MD simulations, a time step of 0.25 fs was employed. For NVT simulations, a Berendsen thermostat with 50 fs damping parameter was used; for NPT simulations, a Berendsen thermostat with 200 fs damping parameter and a Berendsen barostat with 20,000 fs damping parameter were used.

For the Sn-doped ZnO–P₂O₅ glass structures, we choose two models of the host glass from the ten different quenched models generated for each composition, in which the calculated medium range order parameters (connectivity between PO₄ tetrahedra) have in closest agreement with those determined by ³¹P NMR measurements [10, 11]; comparison between the computed and experimental values is presented in following section (see Fig. 3). To take into account local variations in the glass, we randomly replaced one Zn²⁺ site with an isovalent Sn²⁺ dopant, at eight different Zn sites for each host glass model, providing models for 16 different local Sn sites for each composition. The Sn-doped atomic structures initialized in this way were further relaxed using first principles MD (FPMD) simulations at 600 K for 6 ps and additionally at 300 K for 6 ps (1 fs time steps with Nosé-Hoover thermostat) to optimize the coordination environment around the Sn sites. We employed the Heyd-Scuseria-Ernzerhof screened hybrid (HSE06) [18] functionals for the structural optimization to accurately describe the atomic and electronic structures of Sn-doped ZnO–P₂O₅ glass structures; 0.375% of nonlocal Fock-exchange is used, which gives an energy band gap of 3.43 eV for ZnO, similar to the experimental value of 3.44 eV [19]. Finally, the optical spectra including electron-hole interaction were calculated using the Bethe-Salpeter equation (BSE) [20]. All first-principles calculations were performed using the VASP code [21–24], with a plane-wave basis cutoff of 450 eV and using the projector augmented wave method [25] with the Perdew-Burke-Ernzerhof (PBE) [26] and HSE06 [18] functionals.

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