



# Molecular dynamic simulation of interstitial oxide ion migration in $\text{Pb}_{1-x}\text{La}_x\text{WO}_{4+x/2}$ scheelite



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## ABSTRACT

Interstitial oxide ion conducting  $\text{Pb}_{0.7}\text{La}_{0.3}\text{WO}_{4.15}$  scheelite material was synthesized by a traditional high-temperature solid state reaction method and its structure was analyzed by Rietveld method on neutron powder diffraction (NPD) data, which indicates the positional disorder owing to the existence of extra oxygen from donor doping of  $\text{La}^{3+}$  for  $\text{Pb}^{2+}$ . Atomistic static-lattice simulation indicates that interstitial oxygen defects are accommodated via entering into the bonding environment of  $\text{WO}_4$ , resulting in local corner-shared  $\text{W}_2\text{O}_9$  polyhedral units. The molecular dynamic simulations show that the interstitial oxide ion can move among the  $\text{WO}_4$  tetrahedral units through a synergic mechanism involving continuous breaking and reformation of  $\text{W}_2\text{O}_9$  units assisted by rotation and deformation of  $\text{WO}_n$  polyhedra and knock-on process between oxygen atoms.

## 1. Introduction

Oxide ion conductors have important applications in various technologies including solid oxide fuel cells, oxygen sensor, gas separation/permeation and syn-gas production from the oxidation of natural gas [1–4]. Lowering the operating temperatures for these devices requires high oxide ion mobility at low temperature, which has stimulated extensive search for new oxide ion conductor and deep understanding the oxide-ion migration mechanisms. The charge carriers for the oxide ion conduction are either oxygen vacancy or interstitial defects [5]. The occurrence of oxygen vacancy conduction is more common than interstitial oxide ion conduction. The leading oxide ion conductors, yttria-stabilized zirconia [6] and strontium magnesium co-doped lanthanum gallate [7], are based on the cubic or pseudo-cubic high symmetric structures of fluorite and perovskite [1]. Recently high oxide ion conduction has been demonstrated on tetrahedral networks with presence of the interstitial oxygen defects and the lower symmetry [5,8,9]. The typical examples are silicate and germanate apatites [8] and gallate melilites [5], which are composed of isolated tetrahedral units and two-dimensional tetrahedral layers, respectively.

More recently  $\text{LnNbO}_4$  orthoniobate scheelites, which is derived from fluorite but composed of isolated tetrahedral units, attracts interest owing to the interstitial oxide ion conduction [10–12].  $\text{LnNbO}_4$  is a fergusonite phase [13] (a distorted scheelite phase) at room temperature, which transit to the ideal tetragonal scheelite phase at high temperature [14]. The interstitial oxygen atoms can be

introduced into the niobate scheelite structure via oxidation e.g.,  $\text{CeNbO}_{4+x}$  [10,11] or donor substitution e.g.,  $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+x/2}$  [12]. The incorporation of extra oxygen into scheelite results in complex structural relaxation, which it is hardly to describe using the structure solution based on the diffraction techniques that generally address the average structure. So far only the structure of mixed-valent  $\text{CeNbO}_{4.25}$  was experimentally determined [11], featuring the long-range commensurately structural modulation owing to the increase coordination number of Nb and the resultant polyhedral connectivity change as well as the  $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$  ordering. Molecular dynamic (MD) simulations have indicated that oxide ion diffusion in  $\text{CeNbO}_{4.25}$  favor the linked  $\text{NbO}_n$  polyhedral paths [11]. While in donor-substituted  $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+x/2}$ , a knock-on feature among the interstitial and framework oxygen atoms was emphasized by the MD simulations on their high-temperature scheelite phase [15].

Apart from these niobate scheelites above, interstitial oxide ion conduction in donor-substituted  $\text{PbWO}_4$  scheelites also has been attracting attention for more than two decades [16]. When lead ions are partly substituted by lanthanum ions [16,17], such as  $\text{Pb}_{1-x}\text{La}_x\text{WO}_{4+x/2}$ , the solubility range of the La-substituted system was found to expand up to  $x = 0.3$ , the widest solid solution range among the lanthanum-substituted  $\text{PbWO}_4$  [17]. The charge unbalance from the donor substitutions on  $\text{Pb}^{2+}$  sites were supposed to be compensated by creating oxide ion interstitials and high oxide ion conduction appears at elevated temperatures, e.g., oxide ion conductivity of  $\text{La}_{0.2}\text{Pb}_{0.8}\text{WO}_{4.1}$  compositions reached  $\sim 0.04$  S/cm at 800 °C [16].

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The experimental identification of interstitial oxygen defects in donor-substituted  $\text{PbWO}_4$  is a challenging task. Takai et al. [18] tried neutron powder diffraction to search for the position of interstitial oxygen defects in  $\text{Pb}_{0.8}\text{La}_{0.2}\text{WO}_{4.1}$  and proposed a site next to Pb atoms but away from W atoms for the interstitial oxygen without considering the rationality of the local chemical environment for the interstitial oxygen. Thus the interstitial oxygen sites in  $\text{Pb}_{1-x}\text{La}_x\text{WO}_{4+x/2}$  requires further validation. Further detailed information about the local distribution of those excess anions in  $\text{Pb}_{1-x}\text{La}_x\text{WO}_{4+x/2}$  has been investigated using EXAFS of W atoms by Lin et al., which indicated that the coordination number of W in the first coordination shell increases, confirming existence of interstitial oxygen and suggesting incorporation of interstitial oxygen into the  $\text{WO}_4$  tetrahedral units. Chen et al. [19] has performed the first-principles study on  $\text{La}^{3+}$  doping in  $\text{PbWO}_4$  crystal for different doping concentrations, which indicated that the La donor substitution in the lightly and heavily doped  $\text{PbWO}_4$  induces vacancies in Pb sites and interstitial oxygen defects, respectively.

In this work, the interstitial oxygen positions in the La-substituted  $\text{PbWO}_4$  is revisited using the neutron powder diffraction data of  $\text{Pb}_{0.7}\text{La}_{0.3}\text{WO}_{4.15}$  composition with more interstitial oxygen concentration and atomistic simulations are employed to investigate the local defect structure, which is hardly accessible from diffraction data, and to elucidate the migration paths of oxygen interstitials in La-substituted  $\text{PbWO}_4$ . A new cooperative mechanism involving rotation and deformation of  $\text{WO}_4$ , continuous breaking and reforming of corner-sharing  $\text{W}_2\text{O}_9$  units, and a knock-on process between oxygen atoms is presented for the first time for  $\text{PbWO}_4$  scheelite from the molecular dynamic simulations.

## 2. Methods

### 2.1. Synthesis

Polycrystalline  $\text{Pb}_{0.7}\text{La}_{0.3}\text{WO}_{4.15}$  sample was synthesized by conventional high-temperature solid-state reaction method.  $\text{PbCO}_3$  (99.7%, Aladdin),  $\text{H}_2\text{WO}_4$  (99%, Aladdin),  $\text{La}_2\text{O}_3$  (99.99%, Aladdin) were used as raw materials, which were weighed according to the correct stoichiometry and mixed thoroughly in ethanol in agate mortar. The mixed powders were pressed uniaxially into pellets with 12 mm diameter, which were preheated at 200 °C for 140 min in air and then were fired at 1000 °C for 12 h at heating and cooling rates of 5 °C/min.

### 2.2. Characterization

Phase formation was examined by powder X-ray diffraction (XRD) using Panalytical X'pert powder diffractometer using Cu K $\alpha$  radiation. Constant-wavelength neutron powder diffraction (NPD) data was collected at ambient temperature on the BT1 diffractometer at the National Institute of Standards and Technology (NIST). The sample was sealed under helium in a vanadium cell and was measured using the Cu(311) monochromator with a 90° takeoff angle and in-pile collimation of 60 min of arc ( $\lambda = 1.54030 \text{ \AA}$ ). Data was collected over the 2 $\theta$  range of 3–168° with a step size of 0.05°. All diffraction data analyses were performed using the program GSAS [20] under EXPGUI interface [21] by the Rietveld method [22]. The X-ray Energy dispersive spectroscopy (EDS) elemental analysis was performed on the Hitachi (Tokyo, Japan) S4800 scanning electron microscopy (SEM). The sample was coated with gold as a thin conducting layer prior to the EDS elementary analysis.

### 2.3. Atomistic simulations

The static-lattice and molecular dynamic (MD) atomistic simulations were carried out based on the interatomic potential method. The static-lattice simulations were performed using the General Utility Lattice Program (GULP) program [23,24]. The interatomic interactions

between two ions, with distance  $r$ , are represented as ionic, pair-wise potential of the form [25]

$$U_{ij}(r) = \frac{z_i z_j e^2}{r} + A_{ij} \exp\left(\frac{-r}{\rho_{ij}}\right) - \frac{C_{ij}}{r^6}$$

where the first part is the long-range Coulomb term and the latter are the short-range term described by the two-body Buckingham form to model the Pauli repulsions and Van Der Waals attractions between electron clouds [25],  $z_i$  is the formal charge of atom  $i$ , and  $A_{ij}$ ,  $\rho_{ij}$ , and  $C_{ij}$  are the adjustable potential parameters. The shell-model originally developed by Dick and Overhauser [26] is used to describe ionic polarizability ( $\alpha$ ), which treats ion in terms of a massless shell with charge  $Y$  connected via an isotropic harmonic spring with force constant  $k$  to the massive ion core with charge  $z-Y$ , namely,

$$\alpha = \frac{Y^2}{k}$$

The potentials parameters for the atomistic simulations were transferred from previous work [27,28] and tested to reproduce the crystal structure of  $\text{PbWO}_4$ . The defect energies were calculated through the treatment of lattice relaxation around the defect by the Mott-Littleton approach [29] which divides the crystal lattice into two regions: an inner region surrounding the defect and the outer region. The dopant solution energies were then calculated using the interstitial and dopant defect energy terms as well as the lattice energies for the  $\text{La}_2\text{O}_3$  and  $\text{PbO}$  oxides. The MD simulations were performed using the DL\_POLY code [30] in the NVT ensemble with a Berendsen [31] thermostat on an  $8 \times 8 \times 4$  supercell containing 6208 ions (with inclusion of the shell model) and having a composition of  $\text{Pb}_{0.875}\text{La}_{0.125}\text{WO}_{4.0625}$ , on which energy minimizations were performed through zero temperature dynamic simulations for 100 ps prior to the MD simulations at high temperatures. The systems were equilibrated first under a constant pressure of 1 atm for 20 ps before carrying out the main MD simulations at specific temperatures in 700–900 °C temperature region for 2,750,000 time steps with a time step of 0.04 fs (the larger time steps resulted in  $< 3$  link-cell dimension and therefore extremely low parallel computation efficiency which halted the computation at short simulation time  $< 50$  ps). The La dopants and oxygen interstitials were distributed randomly within the simulation box. The Visual Molecular Dynamic package [32] was used to carry out the MD data analysis, and the mean square displacement (MSDs) were calculated with nMoldyn code [33]. Oxygen diffusion coefficients are calculated from the MSD plots as a function of simulation time.

## 3. Results and discussion

### 3.1. NPD structural analysis

The phase formation in the  $\text{La}_{0.3}\text{Pb}_{0.7}\text{WO}_{4.15}$  sample was examined by XRD, which indicates formation of essentially single phase except for minor extra reflections from unknown impurities (Fig. S1). The EDS elemental analysis (Fig. S2) gave an average atomic ratio  $\text{La}_{0.31(4)}\text{Pb}_{0.69(4)}$ , close to the expected La/Pb ratio. Rietveld refinement was performed on the room-temperature NPD data of the  $\text{La}_{0.3}\text{Pb}_{0.7}\text{WO}_{4.15}$  sample based on the structural model in space group  $I4_1/a$  of parent  $\text{PbWO}_4$  [34], which contains one 4b Pb site, one 4a W site, and one 16 f O site. The occupancies of La and Pb sites were refined, giving a  $\text{La}_{0.35(6)}\text{Pb}_{0.65(6)}$  ratio, close to the nominal composition. The refinement of oxygen site occupancy confirms that oxygen sites are fully occupied. In order to locate the extra sites for the interstitial oxygen, difference Fourier map calculation was performed, which however does not show apparent residual nuclear density. Anisotropic atomic displacement parameters (ADPs) were refined and the ellipsoid plot (Fig. 2) suggests positional disorder nature for oxygen and Pb/La atoms in the structure of  $\text{Pb}_{0.7}\text{La}_{0.3}\text{WO}_{4.15}$ . The

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