Contents lists available at ScienceDirect





Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi

Oxygen conductivity in a double-well model for ion jumps in layered perovskite-related oxides



B.V. Politov, S.N. Marshenya, A.Yu. Suntsov*, I.A. Leonidov, V.L. Kozhevnikov

Institute of Solid State Chemistry UB RAS, Yekaterinburg, Russia

ABSTRACT

The theoretical analysis of oxygen-ion conductivity in double perovskite type oxides was performed. The model of ion transport was developed by considering two energetically non-equivalent oxygen positions for ion jumps in the crystalline structure. The temperature variations of oxygen ion conductivity were shown to depend on thermodynamic parameters of the intrinsic oxygen disordering process. The model proposed was verified by experimental data for perovskite-like non-stoichiometric $PrBaCo_2O_{6-\delta}$, $Sr_3Fe_2O_{7-\delta}$ and its titanium-doped derivative.

1. Introduction

The perovskite related mixed conducting oxides of 3d metals have become popular in the development of SOFCs electrodes, oxygen separating membranes and sensors [1-3]. In this relation, significant interest has been attracted in recent years to double perovskite cobaltites $LnBaCo_2O_{6-\delta}$, where Ln is a rare-earth metal, which are currently considered as promising cathode materials for intermediate temperature SOFCs [4,5]. The large size difference results in ordering of Ba and Ln cations and respective doubling of the unit cell with formation of O(I), O(II) and O(III) structurally inequivalent oxygen positions, Fig. 1. The obtained structure can be depicted also as an alternation of Ln-O(I), Co–O(II) and Ba–O(III) metal-oxygen layers along c axis. The robust positions O(III) remain always completely filled so that Ba-O(III) layers are rendered virtually impenetrable for oxygen jumps as strong anisotropy of ion diffusion [6,7] gives evidence to. At the same time, the occupancy of O(I) positions may easily change from zero to unity at variations of ambient temperature and oxygen pressure [8-11]. The energetics of O(II) positions is intermediate. In the result, several per cent of oxygen vacancies can reside in O(II) sites. Though small in number, these vacancies appear to play a crucial role in formation of oxygen migration pathways and bulk ion transport via O(I)-O(II)-O(I) jumps [12-14]. Similar oxygen transport mechanism via minority vacancies was first suggested in the layered Ruddlesden-Popper ferrite Sr₃Fe₂O₇ [15–17].

Authors [14] used classical molecular dynamics for analysis of neutron diffraction data and numerical simulations of ion migration in NdBaCo₂O_{6- δ}. Based on the model of atomic jumps in this work we suggest an alternative consideration of the ion transport over two

* Corresponding author. E-mail address: suntsov@ihim.uran.ru (A.Y. Suntsov).

https://doi.org/10.1016/j.ssi.2018.05.008

inequivalent positions in layered oxides. The utility of the obtained expression for the ionic conductivity is confirmed by a favorable comparison of the calculated results with the experimental data available in the literature.

2. Model

Following [18,19] we can consider the example of quasi-one dimensional oxygen ion transport over O(I) and O(II) positions in presence of external electric field directed along x axis in tetragonal LnBaCo₂O_{6- δ}. The energy barriers for jumps of oxygen vacancies and ions are shown schematically in Fig. 2. The oxygen vacancy flux across a plane separating O(I) and O(II) positions can be presented as

$$J_{V_{\rm O}} = \lim_{\Delta t \to 0} (\Delta n_{V_{\rm O(I)}} / 2\Delta t + \Delta n_{V_{\rm O(II)}} / 2\Delta t) = \frac{J_{V_{\rm O(I)}} + J_{V_{\rm O(II)}}}{2}$$
(1)

Here, $\Delta n_{V_{O(I)}}$ and $\Delta n_{V_{O(I)}}$ stand for the amount of oxygen vacancies that jumped within time interval $t \div t + \Delta t$ from positions O(I) and O (II) while $J_{V_{O(I)}}$ and $J_{V_{O(I)}}$ represent respective net flux values; Δn_i is interrelated with the respective molar concentration [*i*] as $\Delta n_i = r_0 \cdot [i] / V$, where r_0 is the length of the elementary jump and V is the elementary unit volume. Under assumption of weak field, i.e., infinitesimally small disturbance of the defect equilibrium, in the further treatment we can utilize equilibrium concentrations of oxygen species that appear as

$$O_{O(II)}^{X} + V_{O(I)}^{"} = O_{O(I)}^{X} + V_{O(II)}^{"}$$
(2)

at the expense of free energy change ΔG_{od}° . In writing (2) we use Kröger–Vink notation [20]. The transition of an oxygen vacancy $V_{O(1)}^{\circ}$ to a nearby site $O_{O(1)}^{\circ}$ in Fig. 2 can be considered as mediated by formation of

Received 20 March 2018; Received in revised form 7 May 2018; Accepted 8 May 2018 0167-2738/ \odot 2018 Elsevier B.V. All rights reserved.



Fig. 1. The sketch of oxygen ion jumps over O(I) and O(II) oxygen positions in double perovskites.

transition states

$$V_{O(I)}^{"} + O_{O(II)}^{X} = (V_{O(I)}^{"} - O - V_{O(II)}^{"})$$
(3)

$$V_{\rm O(II)}^{..} + O_{\rm O(I)}^{\rm x} = (V_{\rm O(II)}^{..} - O - V_{\rm O(I)}^{..})$$
(4)

where O denotes oxygen in the saddle point between vacant O(I) and O (II) positions. Introducing activation energies $\Delta G_{II}^{\#}$ and $\Delta G_{II}^{\#}$ for reactions (3) and (4), respectively, we see from Fig. 2 that

$$\Delta G_{\rm II}^{\#} = \Delta G_{\rm I}^{\#} - \Delta G_{od}^{\circ} \tag{5}$$

Taking into account fluxes $\vec{J}_{V_{O(1)}}/\vec{J}_{V_{O(1)}}$ created by jumps in the direction along/against the external field [18,19], respectively, we can present the net flux of $V_{O(II)}^{"}$ vacancies in the direction of the external field as

$$J_{V_{O(II)}} = J_{V_{O(II)}} - J_{V_{O(II)}} =$$

$$= \frac{[V_{O(II)}^{\circ}] \cdot [O_{O(I)}^{\circ}] \cdot r_{0} \cdot \nu}{V} \cdot \left\{ \exp\left(-\frac{\Delta G_{II}^{\#} - \Delta G_{od}^{\circ} - \Delta u}{kT}\right) - \exp\left(-\frac{\Delta G_{II}^{\#} - \Delta G_{od}^{\circ} + \Delta u}{kT}\right) \right\}$$
(6)

where ν is the characteristic frequency of jump attempts, k is the Boltzmann constant and T is absolute temperature. The small energy additive Δu can be calculated as

$$\Delta u = ze \frac{d\varphi}{dx} \frac{r_0}{2} \tag{7}$$

where z is charge number, e is elementary charge and $d\varphi/dx$ is electric field gradient. Under assumption $\Delta u \ll kT$ expression (6) can be simplified to

$$J_{V_{\rm O(II)}} = \frac{ze \cdot r_0^2 \cdot [V_{\rm O(II)}^{"}] \cdot [O_{\rm O(I)}^{\times}] \cdot \nu}{kT \cdot V} \exp\left(-\frac{\Delta G_{\rm II}^{\#} - \Delta G_{od}^{\circ}}{kT}\right) \frac{d\varphi}{dx}$$
(8)

In similar manner we can obtain the net flux created by jumps from O(I) positions

$$J_{V_{\mathrm{O}(\mathrm{I})}} = \frac{ze \cdot r_0^2 \cdot [V_{\mathrm{O}(\mathrm{I})}] \cdot [\mathsf{O}_{\mathrm{O}(\mathrm{II})}] \cdot \nu}{kT \cdot \mathrm{V}} \exp\left(-\frac{\Delta \mathrm{G}_{\mathrm{I}}^{\#} + \Delta \mathrm{G}_{od}^{\circ}}{kT}\right) \frac{d\varphi}{dx}$$
(9)

The net oxygen ion current density $j_{V_0} = zeJ_{V_0}$ can be written as the sum of (8) and (9)

$$j_{V_{\mathrm{O}}} = \frac{(ze)^{2} \cdot r_{0}^{2} \cdot \nu}{kT \cdot \mathrm{V}} \begin{cases} [V_{\mathrm{O}(\mathrm{II})}^{..}] \cdot [\mathrm{O}_{\mathrm{O}(\mathrm{I})}^{\times}] \cdot \exp\left(-\frac{\Delta G_{\mathrm{II}}^{\mathrm{H}} - \Delta G_{\mathrm{od}}^{\circ}}{kT}\right) + \\ + [V_{\mathrm{O}(\mathrm{I})}^{..}] \cdot [\mathrm{O}_{\mathrm{O}(\mathrm{II})}^{\times}] \end{cases} \cdot \frac{d\varphi}{dx} \\ \cdot \exp\left(-\frac{\Delta G_{\mathrm{I}}^{\mathrm{H}} + \Delta G_{\mathrm{od}}^{\circ}}{kT}\right) \end{cases}$$
(10)

The equilibrium constant for the disordering reaction (2)



Fig. 2. The energy barriers for oxygen ion jumps over O(I)–O(II)–O(I) positions in presence of external electric field. The length of the elementary jump is $r_0 = a/2$, where *a* is the tetragonal elementary unit parameter.

Download English Version:

https://daneshyari.com/en/article/7744219

Download Persian Version:

https://daneshyari.com/article/7744219

Daneshyari.com