Unraveling the correlation between oxide-ion motion and upconversion luminescence in b-La$_2$Mo$_2$O$_9$:Yb$^{3+}$,Er$^{3+}$ derivatives†

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An optical approach is an alternative method to give insight into the oxide-ion motion in oxide-ion conductors. Herein, we illustrate the correlation between upconversion (UC) luminescence in Yb$^{3+}$–Er$^{3+}$ and oxide-ion motion in a b-La$_2$(Mo,W)$_2$O$_9$ series. The break points at B150 1C in the logarithmic UC emission intensity ratio of 1525/1660 or 1660/1550 (the three emission peaks of Er$^{3+}$) versus temperature imply oxide-ion jumps, whereas the slopes of these plots above 150 1C suggest the capacity of oxide-ion motion. Specifically, the larger the absolute slope values, the higher the oxide-ion conduction capacity. Due to the pinning feature of the Fermi level contributed by the Mo–O bonds in b-La$_2$Mo$_2$O$_9$ both with and without anion-Frenkel defects or W dopants, as revealed by density functional theory calculations, b-La$_2$Mo$_2$O$_9$ remains electronically insulating. Thus, the increase in activation energy and decline in conductivity with an increase in W contents at low temperature (6400 1C) is likely attributed to the higher barrier for the formation of new anion-Frenkel defects. This research gives another perspective on oxide-ion conductors via an optical probe.

Introduction

Oxide-ion conductors are essential for clean electrochemical applications not only in solid oxide fuel cells, but also in oxygen sensors and oxygen separation. Therefore, it is necessary to investigate the thermally driven oxide-ion motion and to understand the long-range oxide-ion conductivity in oxide-ion conductors. A previous report suggested an optical approach to detect oxide-ion swapping in a-La$_2$Mo$_2$O$_9$ in addition to all the available approaches such as internal friction spectroscopy, neutron powder diffraction and simulation, which utilizes the upcon-version (UC) luminescence intensity ratio of the $^2$H$_{11/2}$, $^4$S$_{3/2}$, $^4$F$_{9/2}$ - $^4$I$_{15/2}$ transitions of Er$^{3+}$. An internal reference with the intensity ratio of $^2$H$_{11/2}$ - $^4$I$_{15/2}$ to $^4$S$_{3/2}$ - $^4$I$_{15/2}$ transitions, which is independent of luminescence loss and fluctuations in excitation intensity and thus varies linearly with temperature,

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Experimental

La$_{1}$Y$_{0.06}$Er$_{0.04}$Mo$_{2}$W$_{x}$O$_{9}$ (x = 0, 0.25, 0.75 and 1.25) was synthesized through a traditional solid state reaction according to Fournier et al. Typically, stoichiometric amounts of La$_{2}$O$_{3}$ (99.99%), MoO$_{3}$ (analytical reagent, A.R.), WO$_{3}$ (A.R.), Yb$_{2}$O$_{3}$ (99.99%) and Er$_{2}$O$_{3}$ (99.99%) were mixed thoroughly in an agate mortar. The mixture was first calcined at 500°C for 10 h and then at 970°C for 13 h with intermediate grinding. Sintered ceramics were prepared using the mixed raw materials presintered at 500°C for 10 h as precursors. Then, the precursors were thoroughly mixed with polyvinyl alcohol (PVA) binder solution and pressed under 20 MPa pressure into pellets. Finally, the pellets were sintered at 970°C for 13 h in air. The sintered ceramic pellets for electric testing were B1 mm in thickness and B10 mm in diameter. The phase purity of the ceramics was identified via powder X-ray diffraction (XRD) (Philips PW1830) with a graphite monochromator and Cu Ka irradiation. UC emission spectra were recorded on a Horiba JOBIN YVON iHR 320 spectrofluorometer equipped with a R928 photomultiplier tube as the detector. The excitation light source was a 980 nm laser diode (LD, Coherent Corp.) for the UC measurement. Raman spectroscopy measurements were performed with a Solatron 1260 Impedance/Gain-Phase Analyzer over the frequency range of 0.1–10$^7$ Hz from room temperature to 650 1C in air. Prior to the measurement, gold was pasted on both sides of the ceramic pellets and then heated at 550°C for 40 min in air to obtain the electrodes.

Regarding the geometry relaxation, the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm method was used for all doping and defect supercell calculations.

Results and discussion

XRD patterns and Raman spectroscopy

Fig. 1a presents the room temperature XRD patterns of the La$_2$Mo$_2$W$_x$O$_9$ (x = 0.25, 0.75 and 1.25) samples and the standard XRD patterns of cubic b-La$_2$Mo$_2$O$_9$ (ICSD98871). The inset of Fig. 1a is the enlarged pseudo-cubic (231) diffraction line. It is reported that monoclinic a-La$_2$Mo$_2$O$_9$ has several splitting peaks for the pseudo-cubic reflection (231) at around 2y = 46–491, however, the peaks in the inset appear to be different from that of monoclinic a-La$_2$Mo$_2$O$_9$.

Raman spectroscopy is a powerful tool to give supporting evidence for the b-La$_2$Mo$_2$O$_9$ structure. Fig. 1b shows Raman spectra for La$_2$Mo$_2$W$_x$O$_9$ (x = 0.25, 0.75 and 1.25) at room temperature. The band at 700–1000 cm$^{-1}$ gives information about the structure transformation. There should be a significant change in the structure of b-La$_2$Mo$_2$O$_9$ since there are only two apparent peaks, while for the a-La$_2$Mo$_2$O$_9$ phase there are at least four apparent distinguished peaks. The two peaks at around 869 cm$^{-1}$ (peak 1) and 922 cm$^{-1}$ (peak 2) are broadened or diminished with W doping, which indicates that the doped samples are in the b form. Thus, the cubic structure is stabilized by doping W, which is similar to that in the previous research.

Temperature-dependent UC behaviors and AC impedance spectroscopy

All the samples exhibit bright and shining UC luminescence at room temperature upon excitation with a 980 nm diode laser. The typical UC emission spectra of La$_{1.9}$Y$_{0.06}$Er$_{0.04}$Mo$_{2}$W$_{0.25}$O$_{9}$ recorded at different temperatures are illustrated in Fig. 2a. The green emission peaks at B525 nm and B550 nm are attributed to $^4$H$_{11/2}$ - $^4$I$_{15/2}$ and $^4$S$_{3/2}$ - $^4$I$_{15/2}$, respectively, whereas the red emission peak at B660 nm is ascribed to the $^4$F$_{9/2}$ - $^4$I$_{15/2}$ transitions of Er$^{3+}$. The temperature-dependent UC emission spectra of the other La$_{1.9}$Y$_{0.06}$Er$_{0.04}$Mo$_{2}$W$_x$O$_9$ (x = 0.75 and 1.25) samples are similar to that of La$_{1.9}$Y$_{0.06}$Er$_{0.04}$Mo$_{1.75}$W$_{0.25}$O$_9$.

For the electronic structure calculations of the W-doped La$_2$Mo$_2$O$_9$ with anion(oxide-ion)-Frenkel (a-Fr) pair defects, ultrafine quality and ultrasoft pseudopotentials with a plane-wave cutoff energy of 380 eV were chosen in the CASTEP software package. Reciprocal space integration was performed using Monkhorst–Pack k-point grids of 2 2 2 k-points in the Brillouin zone. The calculations used tolerance settings as follows: total energy lower than 5.0 10$^{-4}$ eV per atom and maximum ionic Hellmann–Feynman force lower than 0.1 eV Å$^{-1}$.
which both the B525 nm peak and B660 nm peak intensities apparently increase.

The absolute emission intensities of lanthanide ions are greatly influenced by many factors, such as grain sizes, light-focussed domain sizes, pumping power density, fluctuation of light source and spectrometer.\(^\text{35-38}\) Therefore, it should be more convincing to use the relative integrated intensity ratios of the three emission peaks of Er\(^{3+}\) (I525, I550 and I660) to evaluate the temperature effect on UC luminescence, as depicted in Fig. 2c. The intensity ratios of I525/I550 and I525/I660 monotonically increase with an increase in temperature, and the intensity ratio of I660/I550 also increases but behaves differently above 150°C. Owing to the small energy gap of about 800 cm\(^{-1}\) between the \(^2\)H\(_{11/2}\) and \(^4\)S\(_{3/2}\) levels, the \(^2\)H\(_{11/2}\) level can be easily populated from the \(^4\)S\(_{3/2}\) level through thermal activation, which leads to a variation in the \(^2\)H\(_{11/2}\) - \(^4\)I\(_{15/2}\) and \(^4\)S\(_{3/2}\) - \(^4\)I\(_{15/2}\) transitions of Er\(^{3+}\) at different temperatures.\(^\text{4,33,34}\)

The intensity ratio versus temperature Ln B 1/T plot should be linear, which is the basis of optical temperature sensing applications and can be understood by the following equation:\(^\text{35-38}\)

\[
R = \frac{I_{525}}{I_{550}} = \left(\frac{N^{2}H_{11/2}}{N^{4}S_{3/2}}\right)^{1/4} = C \exp \left(-\frac{DE}{kT}\right)
\]

where \(R\) is the intensity ratio and I525 and I550 are the integrated intensities of the \(^2\)H\(_{11/2}\) - \(^4\)I\(_{15/2}\) and \(^4\)S\(_{3/2}\) - \(^4\)I\(_{15/2}\) emissions, respectively. \(N^{2}H_{11/2}\) and \(N^{4}S_{3/2}\) represent the population numbers of the \(^2\)H\(_{11/2}\) and \(^4\)S\(_{3/2}\) levels, respectively. DE is the energy gap between the \(^2\)H\(_{11/2}\) and \(^4\)S\(_{3/2}\) levels, \(k\) is the Boltzmann constant, \(T\) is the absolute temperature and \(C\) represents the pre-exponential constant. Herein, the linear behavior is used as an internal reference to characterize the two other lognormal plots of UC emission intensity ratio, as depicted in Fig. 2d and 3a–c. It is obvious that there is an apparent break point at B150°C in all the samples with different concentrations of W. The break point should have some relationship with short-range oxide-ion motion (jump), as evidenced in previous work.\(^\text{4}\) The oxide-ion jump (forming the anion-Frenkel defects) should be on a scale of a few angstroms in the crystal lattice, which could be sensed by the sensitive UC emissions of nearby lanthanide ions. Thus, the break point suggests that Er\(^{3+}\) experiences large chemical environmental variations when the temperature is above 150°C, which is probably ascribed to the thermally-activated oxide-ion motion. To confirm this, AC impedance spectroscopy data of the samples were recorded as a reference for long-range oxide-ion motion. The permittivity value at 10\(^7\) – 10\(^8\) F cm\(^{-1}\) of the electric double layers between electrodes can indicate long-range oxide-ion motion.\(^\text{39}\)

Fig. 2 (a) UC emission spectra of La\(_{1.9}\)Yb\(_{0.06}\)Er\(_{0.04}\)Mo\(_{1.75}\)W\(_{0.25}\)O\(_{9}\) under excitation of a 980 nm laser beam (about B180 mW mm\(^{-2}\)) at various temperatures and (b) the same spectra with normalization at the 550 nm peak. (c) Variations in the integrated UC emission intensity ratios of La\(_{1.9}\)Yb\(_{0.06}\)Er\(_{0.04}\)Mo\(_{1.75}\)W\(_{0.25}\)O\(_{9}\), i.e., ratio(I525/I550) (magenta ball), ratio(I660/I550) (orange square), and ratio(I525/I660) (cyan up-triangle) (the lines are to guide the eye), with temperature and (d) logarithmic plot of the intensity ratio of I525/I550 (Ln(ratio(I525/I550))), I660/I550 (Ln(ratio(I660/I550))) and I525/I660 (Ln(ratio(I525/I660))) as a function of inverse absolute temperature of La\(_{1.9}\)Yb\(_{0.06}\)Er\(_{0.04}\)Mo\(_{1.75}\)W\(_{0.25}\)O\(_{9}\). The lines are fitted.

\(\text{Fig. 3} \) (a–c) Lognormal plots of the intensity ratio of I525/I550(Ln(ratio(I525/I550))) (d–f) Permittivity of the La\(_{1.9}\)Yb\(_{0.06}\)Er\(_{0.04}\)Mo\(_{x}\)W\(_{0.06}\)O\(_{9}\) \((x = 0.25, 0.75\) and 1.25\()\) ceramic pellets as a function of frequency at different temperatures. The La\(_{1.9}\)Yb\(_{0.06}\)Er\(_{0.04}\)Mo\(_{x}\)W\(_{0.06}\)O\(_{9}\) \((x = 0.25, 0.75\) and 1.25\) ceramics all possess a permittivity of B10\(^{-7}\) F cm\(^{-1}\) at 3.00°C. The large permittivities at low frequency are ascribed to the electric double layers between electrodes, which block the oxide-ion motion at a distance of B1 mm (the thickness of the ceramic samples).
This distance should cover plenty of crystal grains (on the micrometer scale) and should be considered as long range. Associating the break points in the plots of Ln B 1/T with permittivity variation, it can be inferred that there is a correlation between the break points and short-range oxide-ion motion. 39 This relationship is also proven by the case of LaGaO3 derivatives with and without oxide-ion conduction, as depicted in Fig. S2 (ESI†).

Actually, the neutron diffraction data for the La2Mo2O9 derivatives in Fig. 4 gives further direct evidence of the oxide-ion jumps at 100–200 °C since the light atom O in the crystal lattice con-tributes largely to the scattering of neutrons and equivalent isotropic temperature factors of O behave distinctly in this temperature range. Furthermore, the conductivity of the grain boundary is of the same magnitude or even higher than that of the grain, as shown in Fig. S1 (ESI†), which suggests that the amorphous grain boundary might have ionic conductivity. The amorphous phase (Fig. S3, ESI†) shows an analogous temperature-dependent UC behaviour in Fig. S4 (ESI†) when doped with Yb3+/Er3+. Actually, the higher conductive amorphous phase is also proven by recent research on La2Mo2O9 nanowires with an amorphous surface. 17

Fig. 5a presents plots of the slopes below and above the break points versus W contents of Fig. 3a–c, in which Ln(R(1525/1660)) and Ln(R(IS60/1550)) show large variations in temperature above the break point (1B150 1C), whereas there is slight change in temperature below the break point. This also manifests that the oxide-ion motion above 150 1C significantly influences the UC behaviors of Er3+. The temperature-dependent grain conductivities of La1.9Yb0.06Er0.04Mo2.89W1.09O9 (x = 0.25, 0.75 and 1.25) are depicted in Fig. 5b. Herein, both electronic and ionic conductivity contribute to the sum value. Fitting the conductivity in the Arrhenius region gives the activation energy. It can be found that the conductivity declines with an increase in W content at a certain temperature, and the activation energy increases. DFT calculations on electronic structure may give some clues to these phenomena.

DFT calculations

It can be clearly seen in Table 1 that substitution of Mo by W has much lower formation energies compared with doping at the La site, which means that W doping can be easily accomplished without much difficulty. This could be attributed to the fact that their valence state is the same and ionic radius similar (difference less than 0.001 nm) based on the LPS concept of Lacorre. 40 This is consistent with the former research on W-doped La2Mo2O9, which showed high compatibility with the lattice and high doping limits that can reach up to 80%; however, the ion conductivity showed no significant variation. 41,42 The formation of a-Fr in W-doped La2Mo2O9 has very distinct results in different positions. Since we only have limited models on W-doped La2Mo2O9, based on the former research results, we believe that the model with a high formation energy of up to 4.992 eV could be a very special case and hard to realize in actual experiment.

Table 1. Formation energy of W doping in different positions and with a-Fr pair defects

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formation energy (eV)</th>
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</thead>
<tbody>
<tr>
<td>La2Mo1.5W0.5O9</td>
<td>6.854</td>
</tr>
<tr>
<td>La2Mo1.5W0.5O9-a-Fr</td>
<td>0.709</td>
</tr>
<tr>
<td>La2Mo1.5W0.5O9-a-Fr</td>
<td>0.191</td>
</tr>
</tbody>
</table>
This research correlates the UC emission of Er$^{3+}$ with oxide-ion motion in b-La$_2$(Mo,W)$_2$O$_9$. Associating the break points in the plots of Ln B I/T with permittivity variation, the break points should be ascribed to short-range oxide-ion motion. Also, the behaviors (slopes) of the plots above the temperature of the break points reflect long-range oxide-ion motion. The incorporation of W will increase the barrier for formation of new a-Fr defects, resulting in a higher activation energy and lower ion conductivity at low temperature (0400 IC).

Conclusions

This research correlates the UC emission of Er$^{3+}$ with oxide-ion motion in b-La$_2$(Mo,W)$_2$O$_9$. The variation in conductivity shown in Fig. 5b should be mainly due to the change in ion conduction. Considering the capacity of oxide-ion motion (permittivity) in Fig. 3a, the incorporation of W will increase the barrier of formation for new a-Fr defects, resulting in higher activation energy and lower ion conductivity at low temperature (0400 IC).

Conflicts of interest

There are no conflicts of interest to declare.

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