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Structural studies on W^{6+} and Nd^{3+} substituted $La_2Mo_2O_9$ materials

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Abstract

The structure of a series of new ionic conductors based in lanthanum molybdate ($La_2Mo_2O_9$) has been investigated using transmission electron microscopy (TEM), high-resolution X-ray diffraction (XRD) and differential scanning calorimetry (DSC). The superstructure $2a_c \times 3a_c \times 4a_c$ of the low temperature α-polymorph relative to the β-polymorph was confirmed by HRTEM imaging and electron diffraction. Furthermore, the effects of partial cation substitution in the $La_{2-x}Nd_xMo_2O_9$ and $La_2Mo_{2-y}W_yO_9$ series have been also evaluated in the search of new clues to understand the structure and stabilisation of the high temperature and better conductor β-polymorph. The thermal analysis studies show that Nd-substitution does not stabilise completely the β-polymorph at room temperature, although no superstructure ordering was observed by both XRD and HRTEM. On the other hand, W-substitution stabilises the cubic β-polymorph for $y > 0.25$, although, electron diffraction indicates a slight distortion from the cubic symmetry for low W-content. This distortion disappears as the W content increases and the Rietveld refinements gradually render better results.
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1. Introduction

Oxide ion conductors are materials with a number of important applications such as oxygen sensors, dense ceramics for oxygen separation and fuel cell components. Fuel cells are electrochemical devices that convert directly chemical energy into electricity and promise important advantages in comparison to the current technologies based on the combustion of fossil fuels, because they are environmentally friendly and render higher efficiencies [1–4].

Fuel cells require materials exhibiting high ion oxide mobility, which in turn implies very specific structural features only met for a restricted number of solids. The most widely used solid electrolyte nowadays is yttria-stabilised zirconia (YSZ), which is a very good oxide ion conductor at high temperature (typically $0.1\,S\,cm^{-1}$ at 1273 K) and stable for prolonged operation times [5]. However, the high operation temperatures (1000–1273 K) limit the choice of stable materials for the other SOFC components, hence increasing the costs of production.

Over the last two decades, other ionic conductors such as rare-earth doped ceria and $LaGaO_3$-based phases have been studied and developed based upon fluorite or perovskite structures, respectively, showing higher conductivity than YSZ at lower temperatures [6–10]. Unfortunately, they present other drawbacks such as high cost or residual electronic conductivity that must be overcome. Therefore, an electrolyte with very high conductivity at relatively low temperatures is highly demanded to produce efficient fuel cells operating at intermediate temperatures (IT-SOFCs).

Since the discovery of very high oxide-ion conductivity in $La_2Mo_2O_9$ by Lacorre et al., much attention has been directed towards molybdate-based materials due to their potential applications as electrolyte [11]. This compound was first synthesised by Fournier et al. in 1970 [12],

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although the reports on the structural characterisation and the high ionic conductivity are more recent [13,14]. The very high oxide ion conductivity in $La_2Mo_2O_9$ has been explained using the lone pair substitution (LPS) concept, which considers that the partial substitution of lone-pair cations by other cations without lone-pair electrons may generate intrinsic-vacancies in the anionic sublattice [15].

$La_2Mo_2O_9$ undergoes a structural phase transition from the slightly monoclinic α-polymorph to the much better conductor cubic β-polymorph (isostructural to β-$SnWO_4$) at 833 K. This transition is similar to those reported in other fast ionic conductors such as Bi_2O_3 and $Bi_2V_4O_{11}$ and is usually associated to a rearrangement in the oxygen sublattice [16,17].

The applicability of $La_2Mo_2O_9$ is limited by the $\alpha \leftrightharpoons \beta$ phase transition and by its stability under reducing conditions. The partial substitution of either La^{3+} or Mo^{6+} by cations such as Bi^{3+}, Ca^{2+}, Sr^{2+}, Y^{3+} and W^{6+} seems to stabilise the cubic polymorph at room temperature, whilst Nd^{3+} has been reported to adopt the monoclinic superstructure [14,18–22]. Recent reports suggest that $La_2Mo_{2-x}W_xO_9$ phases can be used as SOFC electrolytes, although only at low temperature and under moderate reducing conditions. The introduction of tungsten enhances the stability range and prevents the presence of residual electronic conductivity [23–26].

In the present work, $La_2Mo_2O_9$, $(La,Nd)_2Mo_2O_9$ and $La_2(Mo,W)_2O_9$ phases have been studied by high resolution X-ray diffraction (XRD), transmission electron microscopy (TEM) and thermal analysis to give a further insight of these structures.

2. Experimental

The synthesis of $La_2Mo_2O_9$ (LMO), $La_2Mo_{2-y}W_yO_9$ (LMW) and $La_{2-x}Nd_xMo_2O_9$ (LNM) series was carried out using a freeze-dried precursor method. The starting materials were La_2O_3, Nd_2O_3 (99.99% Aldrich), WO_3 and MoO_3 (99.5% Aldrich). The experimental procedure for the preparation of the freeze-dried precursor powders has been described in detail in previous publications [16,27]. Lanthanum and neodymium oxides were dissolved in diluted nitric acid, and tungsten and molybdenum in diluted ammonia. The solutions were mixed in stoichiometric ratios and then cooled in liquid nitrogen and freeze-dried for 2 days.

A single phase can be obtained after the calcination of the dried precursor powders in air at 673–773 K, although in the present work all samples were calcined between 1123 and 1273 K for 5 h to obtain high crystallinity and to facilitate the structural characterisation. Samples were cooled slowly, i.e. 1–2 K/min in air, to obtain the targeted oxygen stoichiometry and the crystal lattice as close as possible to the equilibrium conditions at room temperature. The samples are labelled as LMO for $La_2Mo_2O_9$ and "Ndx" and "Wy" for $La_{2-x}Nd_xMo_2O_9$ and $La_2Mo_{2-y}W_yO_9$ series, respectively.

XRD patterns were obtained from a Philips X′Pert Pro automated diffractometer, equipped with a primary monochromator and an X′celerator detector. The scans were performed in high resolution mode in the 2θ range from 5° to 120° (step 0.0085–0.016° and 100–500 s/step), using copper $K_{\alpha 1}$ radiation. High-temperature XRD studies were carried out in air, using an Anton Paar TTK 450 Camera, ranging from room temperature to 1123 K. Rietveld refinement of the XRD patterns were performed using FULLPROF software [28]. The fits were performed using a pseudo-Voigt peak-shape function. In the final cycles, the usual profile parameters (scale factors, background coefficients, zero-points, half-width, pseudo-Voigt and asymmetry parameters for the peak-shape) were refined. The occupation numbers and isotropic temperature factors were refined separately due to their strong correlation. All graphics related with XRD patterns were performed using WinPLOTR software [29].

Selected area electron diffraction (SAED) and HRTEM imaging were performed on a JEOL JEM 2011 electron microscope equipped with a (±20°) double-tilt sample holder operating at 200 kV. The equipment used an Oxford Link detector to perform EDS analysis. Samples for TEM observation were prepared by dispersion of a very fine ground powder specimen onto a perforated carbon film supported on a Cu grid. Image simulation was carried out using MacTempas software (v. 3.1.1).

Thermal analysis TG/DTA, differential scanning calorimetry (DSC) and dilatometric measurements were recorded with Perkin Elmer Instruments (Pyris Diamond series) in static air at heating/cooling rate of 5–20 K/min.

Dense pellets of 10 mm diameter and 2 mm thick were pressed at 100 MPa and sintered at 1223–1373 K for 5 h for the electrical characterisation. The relative density of these pellets was higher than 98%. Some reference specimens of commercial yttria stabilised zirconia (8%YSZ, Tosoh) and gadolinium-doped ceria (CGO, Rhodia) were also prepared into pellets and sintered at 1673 and 1773 K, respectively for 10 h. A sample of $La_{1.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.8}$ was also prepared by solid-state reaction and sintered at 1673 K for 10 h. The overall electrical conductivity was measured by impedance spectroscopy, using a 1260 Solartron frequency response analyser in the frequency range from 0.1 Hz to 1 MHz and temperature range from 573 to 1173 K. All samples were measured in the same environmental conditions to compare their conductivity values. The experimental details are reported elsewhere [23,24].

3. Results and discussion

3.1. XRD characterisation

As mentioned in the introduction, it is well known that $La_2Mo_2O_9$ undergoes a phase transition from the monoclinic α-polymorph to the cubic β-$La_2Mo_2O_9$ at 833 K, which is accompanied by a great enhancement of

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