



Stability against reduction of fluorite-like rhombohedral $\text{La}_{5.5}\text{MoO}_{11.25}$ and $\text{Ho}_{5.4}\text{Zr}_{0.6}\text{MoO}_{12.3}$ fluorite: Conductivity and neutron diffraction study

S.N. Savvin^{a,b}, M. Avdeev^c, I.V. Kolbanev^d, E.P. Kharitonova^e, L.G. Shcherbakova^d,
A.V. Shlyakhtina^{d,*}, P. Nuñez^a

^a Department of Inorganic Chemistry, Institute of Materials and Nanotechnology, University of La Laguna, 38200 La Laguna, Tenerife, Spain

^b Department of Chemistry, University of Liverpool Crown Street, Liverpool L69 7ZD, United Kingdom

^c Australian Centre for Neutron Scattering, Australian Nuclear Science and Technology Organisation, Locked Bag 2001, Kirrawee DC, NSW 2232, Australia

^d Semenov Institute of Chemical Physics, Russian Academy of Sciences, ul. Kosygina 4, Moscow 119991, Russia

^e M.V. Lomonosov Moscow State University, Leninskie gory 1, Moscow 119991, Russia

ARTICLE INFO

Keywords:

Fluorite
Rhombohedral phase
Proton-conducting membranes
Resistance to reduction

ABSTRACT

Zr-substituted rare-earth molybdates $\text{Ho}_{5.4}\text{Zr}_{0.6}\text{MoO}_{12.3}$ and unsubstituted $\text{La}_{5.5}\text{MoO}_{11.25}$ demonstrate appreciable mixed electron-proton conductivity in the 200–470 °C and 145–730 °C temperature range, respectively, under wet oxidizing and mild reducing conditions (air, Ar, Ar-5% H_2). Rhombohedral fluorite-like $\text{La}_{5.5}\text{MoO}_{11.25}$ showed the highest bulk conductivity of about 1×10^{-5} S/cm at 400 °C in wet air and Ar. Its impedance spectra did not provide any evidence of the grain boundary contribution in wet atmosphere. Total conductivity of $\text{Ho}_{5.4}\text{Zr}_{0.6}\text{MoO}_{12.3}$ fluorite is much lower and is 3×10^{-7} S/cm at 400 °C in wet air. Besides, it should be noted that there is a grain-boundary contribution of $\text{Ho}_{5.4}\text{Zr}_{0.6}\text{MoO}_{12.3}$ in wet air and Ar.

Thermogravimetry data demonstrate that the fraction of strong structurally bound water and interstitial protons in $\text{La}_{5.5}\text{MoO}_{11.25}$ and $\text{Ho}_{5.4}\text{Zr}_{0.6}\text{MoO}_{12.3}$ is ~0.02–0.03% in the range ~600–900 °C.

The stability of $\text{Ho}_{5.4}\text{Zr}_{0.6}\text{MoO}_{12.3}$ fluorite structure and fluorite-like rhombohedral $\text{La}_{5.5}\text{MoO}_{11.25}$ structure in extremely dry conditions under dynamic vacuum of 10^{-6} – 10^{-7} mbar was investigated by *in situ* variable temperature neutron diffraction between 800 and 1400 °C to understand phase behaviour under mild reducing conditions in a wide temperature range.

Rhombohedral fluorite-like $\text{La}_{5.5}\text{MoO}_{11.25}$ has been shown to be more resistant to reduction under vacuum below 1100 °C in heating–cooling cycles than is fluorite $\text{Ho}_{5.4}\text{Zr}_{0.6}\text{MoO}_{12.3}$. Given the higher proton conductivity of $\text{La}_{5.5}\text{MoO}_{11.25}$, this suggests that rhombohedral fluorite-like $\text{La}_6\text{MoO}_{12}$ -based molybdates are suitable for long-term use under mild reducing conditions and 600–800 °C.

1. Introduction

Currently there is growing research interest in compounds and solid solutions based around tungstate and molybdate systems Ln_2O_3 - MoO_3 and Ln_2O_3 - WO_3 , which primarily arises from their various physical properties (luminescent materials [1–7], catalysts [8], oxygen-ion and proton conductors [9–15]).

These systems already attracted considerable research interest [16–25] about 60 years ago, which was related predominantly to phase diagram studies and structure determination for the large number of various compounds existing in these systems. The La_2O_3 - MO_3 (M = Mo, W) systems aroused the most interest and, accordingly, have been the subject of extensive studies. Results reported by different groups [11,26–29] are rather contradictory because in these systems,

equilibrium is difficult to reach and a number of compounds are stable only in particular temperature or oxygen pressure ranges. In particular, nine compounds are known to exist in the La_2O_3 - MoO_3 system at 1200 °C, but two of them exist only in a certain range of low oxygen partial pressure and cannot be obtained in air [30]. The tungstate system La_2O_3 - WO_3 is known to contain eight compounds forming in air [25].

With decreasing rare-earth ionic radius, the number of compounds decreases, e.g. in the Y_2O_3 - MoO_3 system shown to contain only seven distinct phases [31]. At the same time, three compounds of similar composition are known to exist in the holmia-rich part of the Ho_2O_3 - WO_3 system: $\text{Ho}_6\text{WO}_{12}$ (3:1), $\text{Ho}_{10}\text{W}_2\text{O}_{21}$ (5:2), $\text{Ho}_{14}\text{W}_4\text{O}_{33}$ (7:4) [32,33]. Ho_2O_3 content decreases slightly from $\text{Ho}_6\text{WO}_{12}$ (3:1) to $\text{Ho}_{14}\text{W}_4\text{O}_{33}$ (7:4). These compounds have rhombohedral ($\text{Ho}_6\text{WO}_{12}$ and

* Corresponding author.

E-mail address: annash@chph.ras.ru (A.V. Shlyakhtina).

$\text{Ho}_{14}\text{W}_4\text{O}_{33}$) or tetragonal ($\text{Ho}_{10}\text{W}_2\text{O}_{21}$) fluorite-related structures [23,32]. As was shown in later structural studies [33,34], $\text{Y}_{10}\text{W}_2\text{O}_{21}$ has an orthorhombic rather than a tetragonal structure (Y is similar in ionic radius to Ho). The $\text{Ln}_{10}\text{W}_2\text{O}_{21}$ (Ln = Nd–Ho, Y) compounds were reported to be unstable on cooling [23].

It is clear from general considerations that fluorite ($Fm\bar{3}m$) phases undergoing no phase transitions should be more stable on heating and cooling than distorted and/or oxygen ordered phases with a rhombohedral, tetragonal, or orthorhombic fluorite-related structure are. Indeed, as shown earlier [13] cubic molybdates $\text{Nd}_{5.4}\text{Zr}_{0.6}\text{MoO}_{12.3}$, $\text{Sm}_{5.4}\text{Zr}_{0.6}\text{MoO}_{12.3}$ and $\text{Dy}_{5.4}\text{Zr}_{0.6}\text{MoO}_{12.3}$ with the fluorite structure retain their cubic structure after several heating–cooling cycles in oxidizing or reducing media, although their unit-cell volume slightly decreases after reduction. However the grain-boundary resistance in these samples limited its total conductivity in a wet atmosphere (air, Ar) [35]. It is worth recalling that Zr-doped $\text{Ln}_6\text{MoO}_{12}$ based molybdates ($\text{Nd}_{5.4}\text{Zr}_{0.6}\text{MoO}_{12.3}$, $\text{Sm}_{5.4}\text{Zr}_{0.6}\text{MoO}_{12.3}$, $\text{Dy}_{5.4}\text{Zr}_{0.6}\text{MoO}_{12.3}$) demonstrate appreciable mixed electron-proton conductivity in the low and intermediate temperature range under wet oxidizing and mild reducing conditions [13,14].

MoO_3 and WO_3 volatility in the rare-earth molybdates and tungstates has been the subject of intense discussion in the literature. It has been shown that the normally volatile MO_3 ($M = \text{Mo}, \text{W}$) show exceptional thermal stability in these $\text{Ln}_6\text{WO}_{12}$ and $\text{Ln}_6\text{MoO}_{12}$ rhombohedral compounds [36]. Millet et al. [37] reported that the vaporization of WO_3 from $\text{Ln}_6\text{WO}_{12}$ was 10^6 times lower than it was from free WO_3 . Phase equilibria results indicate that the most stable against reduction Mo (VI) compound in the $\text{Ln}_2\text{O}_3 - \text{MoO}_3$ (Ln = Nd, Pr, Sm) systems is $\text{Ln}_6\text{MoO}_{12}$ with the highest Ln/Mo ratio [38]. Indeed, the rhombohedral fluorite-related phase $\text{La}_{5.8}\text{Zr}_{0.2}\text{MoO}_{12.1}$ proved to be the most stable during thermal cycling under oxidizing or reducing conditions among the Zr-doped rare-earth molybdates $\text{La}_{5.8}\text{Zr}_{0.2}\text{MoO}_{12.1}$, $\text{Nd}_{5.4}\text{Zr}_{0.6}\text{MoO}_{12.3}$, $\text{Sm}_{5.4}\text{Zr}_{0.6}\text{MoO}_{12.3}$, and $\text{Dy}_{5.4}\text{Zr}_{0.6}\text{MoO}_{12.3}$ [13,35]. In contrast to zirconium-doped neodymium, samarium, and dysprosium molybdates $\text{Nd}_{5.4}\text{Zr}_{0.6}\text{MoO}_{12.3}$, $\text{Sm}_{5.4}\text{Zr}_{0.6}\text{MoO}_{12.3}$, and $\text{Dy}_{5.4}\text{Zr}_{0.6}\text{MoO}_{12.3}$ with fluorite structure, rhombohedral fluorite-like $\text{La}_{5.8}\text{Zr}_{0.2}\text{MoO}_{12.1}$ had no grain boundary contribution not only in dry but also in wet atmospheres [35]. In the same study it was found that $\text{La}_{5.8}\text{Zr}_{0.2}\text{MoO}_{12.1}$ ceramic grains had twin core-shell microstructure.

Overall, in the $\text{Ln}_2\text{O}_3\text{-MO}_3$ ($M = \text{Mo}, \text{W}$) systems under consideration, compounds or solid solutions with a fluorite or rhombohedral structure or materials having a core-shell microstructure built of crystallographically similar phases (rhombohedral and fluorite) are best suited for thermal cycling under oxidizing and reducing conditions.

In the present work, lanthanide molybdates were investigated in which the lanthanide cation (La, Ho) is stable in only one oxidation state Ln^{3+} . In this work we report synthesis, crystal structure and conductivity under different oxygen partial pressures of the $\text{Ho}_{5.4}\text{Zr}_{0.6}\text{MoO}_{12.3}$ molybdate with fluorite structure $Fm\bar{3}m$ which is potential intermediate-temperature mixed electron-proton conductor. For comparison, the total conductivity of an unsubstituted fluorite-like $\text{La}_{5.5}\text{MoO}_{11.25}$ with complex rhombohedral structure was also measured in the different atmospheres. The crystal structural evolution of solid solutions $\text{Ho}_{5.4}\text{Zr}_{0.6}\text{MoO}_{12.3}$ and $\text{La}_{5.5}\text{MoO}_{11.25}$ was studied by *in situ* neutron diffraction during thermal cycling in the range 800–1400–800 °C in a vacuum furnace.

The purpose of this work is to compare the stability of rare-earth molybdates belonging to two distinct structural types - fluorite $\text{Ho}_{5.4}\text{Zr}_{0.6}\text{MoO}_{12.3}$ and fluorite-like rhombohedral $\text{La}_{5.5}\text{MoO}_{11.25}$ - under harsh conditions: vacuum and high temperatures, up to 1100 or 1400 °C. Such conditions (high temperatures up to 1100 °C and high vacuum from $\sim 10^{-7}$ to 10^{-6} mbar) are similar to prolonged exposure of the molybdates to temperatures from 600 to 800 °C in a moderately reducing medium, i.e. under typical operating conditions of SOFCs. The extreme conditions - high temperatures up to 1400 °C and high vacuum from $\sim 10^{-7}$ to 10^{-6} mbar - are needed to gain insight into possible

phase transitions of the solid solutions under study, connected with the reduction process.

2. Experimental

$\text{La}_{5.5}\text{MoO}_{11.25}$ and $\text{Ho}_{5.4}\text{Zr}_{0.6}\text{MoO}_{12.3}$ were prepared by the mechanical activation method. After preheating the starting Ln_2O_3 (La, Ho) oxides at 1000 °C for 2 h, they were mixed with the rest of the components (ZrO_2 , MoO_3) and co-milled in the SPEX8000 ball mill for 1 h. MoO_3 was activated prior to co-milling in the high energy Aronov ball mill for 4 min. The mechanically activated mixtures of the oxides were uniaxially pressed at 680–914 MPa and sintered at 1600 °C for 3 h. The geometric density with respect to theoretical value of the as-prepared ceramics $\text{La}_{5.5}\text{MoO}_{11.25}$ and $\text{Ho}_{5.4}\text{Zr}_{0.6}\text{MoO}_{12.3}$ was 91.1 and 89.6%, respectively. All samples were characterized both structurally and electrically.

The microstructure of the sintered ceramics was examined using scanning electron microscopy (JEOL JSM-6390LA). Prior to taking images the ceramic sample $\text{Ho}_{5.4}\text{Zr}_{0.6}\text{MoO}_{12.3}$ was manually ground, polished with diamond paste and finally thermally etched at 1450 °C for 0.5 h.

Thermogravimetric analysis was performed by using the NETZSCH STA 449C system (30–1000 °C, heating rate of 10 K/min, Al_2O_3 plate) in air. Massive ceramic samples (800–1100 mg) were used to detect a weak weight loss effect. The correction curve of an empty measuring cell was previously measured to remove the effect of an illusory increase in weight due to a decrease in the density of air when heated. Several successive heating steps were performed for samples under investigation. In our weight loss measurements, the uncertainty due to contributions left out of account by the correction curve (drift of the balance, initial measurement conditions, etc.) is $\pm 0.02\%$ per heating or cooling cycle.

Electrical conductivity of the samples was studied by impedance spectroscopy. Prior to taking measurements, both faces of the ceramic pellets prepared as described above were covered by Pt paste (Metalor, # 6695) and fired at 950 °C for 1 h. Afterwards, each pellet was settled in a gas-tight sample stage outfitted with an outer ceramic housing, gas inlet and outlet tubes and a thermocouple located in the close vicinity of the sample. The temperature dependence of the total (electronic and ionic) grain bulk conductivity in different dry and wet atmospheres (air, Ar, Ar-5% H_2) was extracted from impedance spectra obtained using a Solartron 1260 frequency response analyzer. The spectra were recorded in the frequency range of 0.1 Hz to 1 MHz on cooling from 850 °C to 250 °C; the root mean square ac voltage amplitude was set to 150 mV. Depending on the atmosphere and temperature it took from 2 to 5 h for the samples to reach the equilibrium conductivity values. Relative humidity of the gases fed into the sample stage was controlled by passing them over a freshly dehydrated silica gel (designated “dry”) or through a water saturator held at 20 °C (designated “wet”), which ensured constant humidity of about 0.023 atm (2.3% H_2O). The impedance spectra obtained under mild reducing (Ar) and oxidizing (air) conditions were fitted to an equivalent circuit consisting of two parallel (RQ) elements placed in series, which represented bulk and electrode contributions to conductivity. For $\text{Ho}_{5.4}\text{Zr}_{0.6}\text{MoO}_{12.3}$ one additional semi-circle appeared in wet Ar and air. In these cases the equivalent circuit was modified accordingly in order to take into account the presence of the grain boundary contribution.

In situ variable temperature neutron diffraction data were collected on the high-resolution powder diffractometer ECHIDNA at the OPAL research reactor (Australian Nuclear Science and Technology Organisation) using neutrons with the wavelength of 2.4395 Å. The as-prepared pellets of $\text{La}_{5.5}\text{MoO}_{11.25}$ and $\text{Ho}_{5.4}\text{Zr}_{0.6}\text{MoO}_{12.3}$ were suspended in a vacuum furnace on a platinum wire and diffraction data were collected under dynamic vacuum in the range 10^{-6} – 10^{-7} mbar on heating with the rate of 20 °C/min from room temperature to 1400 °C and subsequent cooling. At each temperature, on reaching the

Download English Version:

<https://daneshyari.com/en/article/7744370>

Download Persian Version:

<https://daneshyari.com/article/7744370>

[Daneshyari.com](https://daneshyari.com)