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Extension of the $La_7Mo_7O_{30}$ structural type with $La_7Nb_3W_4O_{30}$ and $La_7Ta_3W_4O_{30}$ compounds

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Abstract

Two compounds of formula $La_7A_3W_4O_{30}$ (with A = Nb and Ta) were prepared by solid-state reaction at 1450 and 1490 °C. They crystallize in the rhombohedric space group R-3 (No. 148), with the hexagonal parameters: $a = 17.0640(2)$ Å, $c = 6.8859(1)$ Å and $a = 17.0701(2)$ Å, $c = 6.8851(1)$ Å. The structure of the materials was analyzed from X-ray, neutron and electronic diffraction. These oxides are isostructural of the reduced molybdenum compound $La_7Mo_7O_{30}$, which are formed of perovskite rod along [111]. An order between (Nb, Ta) and W is observed.

Keywords: Perovskite; X-ray and neutron diffraction; Electron microscopy; BVS

1. Introduction

Oxide ion conductors still attract attention due to their potential application in solid-oxide fuel cell. These oxides belong to only a few number of structural families [1]: fluorite type (stabilized zirconia, δ-Bi_2O_3), perovskite (doped $LaGaO_3$, $Ba_2In_2O_5$), intergrowth perovskite/Bi_2O_2 slabs (BIMEVOX) and pyrochlore ($Gd_2Ti_2O_7$). More recently, new structural types have shown good oxide ion conduction. We can cite our work on $La_2Mo_2O_9$ [2,3] which has no structural relation to any other structural type or the more conventional Apatite structure $La_{9.33}Si_6O_{26}$ [4].

As an extension to the stabilized zirconia, solid-state chemists have explored structures related to fluorite type, mainly the Scheelite structure. Some recent works on $Pb_{1-x}La_xW_{4+x/2}$ [5,6], $CeTaO_4$ [7] and $BiVO_4$ [8] have been reported. But attention to related Scheelite structure is even more ancient compared with the work on excess Scheelite-based compounds $La_{1-x}Th_xNbO_{4+x/2}$ and $LaNb_{1-x}W_xO_{4+x/2}$ examined by Cava et al. [9]. From this study a compound of formula $LaNb_{0.4}W_{0.6}O_{4.3}$ was reported without structural information's.

Here, we present the synthesis, physical and structural characterization of two new phases with the formula $La_7Nb_3W_4O_{30}$ and $La_7Ta_3W_4O_{30}$, which are isostructural of the reduced molybdate phases $La_7Mo_7O_{30}$ [10].

2. Experimental

The room temperature and thermal X-ray diffraction patterns were collected on a Bragg-Brentano diffractometer (MPD-PRO Panalytical) equipped with a linear detector X'Cellerator and an Anton Paar HTK12 furnace. For the structural analysis, the diffraction pattern was collected in the range (10°–145° (2θ)), with an increment step of 0.017° (2θ) and a total collecting time of 5.33 h. The thermal X-ray diffraction patterns were collected during one night. The neutron diffraction

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patterns of $La_7Ta_3W_4O_{30}$ and $La_7Nb_3W_4O_{30}$ were collected on the Debye-Sherrer diffractometer D1A (instrument at ILL, Grenoble). Data collection was performed at ~1.911 Å on ~15 g of compound. For the patterns the increment step was 0.05° (2θ), interval of data collection ranging from 0° to 162°, the total counting time was ~6 h for $La_7Ta_3W_4O_{30}$ and ~2 h for $La_7Nb_3W_4O_{30}$.

The electron diffraction study was performed on a 200 kV side entry JEOL2010 transmission electron microscope with a double-tilt specimen holder operating at room temperature. For specimen preparation, a small amount of powder was ground in an agate mortar and pestle under dry methanol to produce a suspension. A drop of the suspension was deposited on a holey carbon film supported by a 1000 mesh copper grid and dried.

The density measurements were carried out on a gas pycnometer ACCUPIC 1330 (Micromeritics) with helium as gas. The temperature of measurement was 24 °C ± 1 °C, for each measurement an amount of approximately 200 mg was used.

The transport property was studied by impedance spectroscopy using a Schlumberger Solartron SI 1260 frequency response analyzer with 0.1 V amplitude signal over the 32 MHz–0.1 Hz frequency range. Pellets of 10 mm diameter were used for measurements with, as electrodes, platinum deposited on both faces.

3. Results and discussion

3.1. Synthesis

Different compounds were prepared with La_2O_3, Nb_2O_5 and Ta_2O_5 and WO_3 as starting oxides. Lanthanum oxide powder was dried and decarbonated at 1000 °C overnight prior to use. The first attempt of synthesis was done with the nominal composition $LaNb_{0.4}W_{0.6}O_{4.3}$ as mentioned by Cava et al. [9] at 1400 °C for one night (see Fig. 1). The same five strongest lines were obtained in the powder pattern: $d = 4.263$, 3.221, 2.928, 2.637 and 1.984 Å. The structure is isotypic with $La_7Mo_7O_{30}$, this feature was found after the electron diffraction analysis. Nevertheless, both the compositions are closed, the compound $LaNb_{0.4}W_{0.6}O_{4.3}$ presents 60 mol% of $LaWO_{4.5}$ and $La_7Nb_3W_4O_{30}$ presents 57.1 mol% of $LaWO_{4.5}$. Subsequently, $La_7A_3W_4O_{30}$ (with A = Nb and Ta) compounds were synthesized from the stoichiometric composition of oxides. The weighted powders were ground in an agate mortar for few minutes and then placed in an alumina crucible. Finally, the powders were heated for one night at 1450 °C and 1490 °C, respectively, for $La_7Nb_3W_4O_{30}$ and $La_7Ta_3W_4O_{30}$; no particular condition was used in order to cool down the samples. The final compounds were obtained in white color.

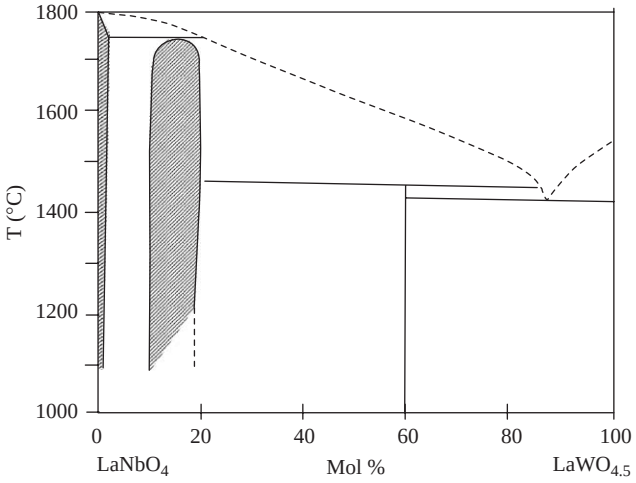

Fig. 1. Phase equilibrium diagram for the system $LaNbO_4$–$LaWO_{4.5}$ (from Ref. [9], solid solution domain is hatched for clarity).

3.2. Electron diffraction and high resolution electron microscopy

As for the analysis of $La_7Mo_7O_{30}$ [10], the first reciprocal lattice reconstruction, performed by electron diffraction, which allowed us to determine the cell parameters in the wrong monoclinic subcell was as follows:

$$a \approx 10.4,\ b \approx 17.2,\ c \approx 6.6,\ \text{and}\ \beta \approx 110°.$$

The observed reflection condition during the reciprocal lattice reconstructions was hkl: $h + k = 2n$, leading to the monoclinic space groups: $C2/m$. The true hexagonal lattice was deduced from the observation of electron diffraction pattern along the [001]* hexagonal cell as shown in Fig. 2, and from our previous experience. No extra reflection dots involving the doubling of the c parameter was observed, this was also the case in $La_7Mo_7O_{30}$ electron diffraction analysis. High-resolution electron microscopy images were measured along [001] direction, a very periodic contrast was observed in the whole crystal attesting of the nice ordering of the structure (Fig. 3). The same feature was also evidenced in the $La_7Mo_7O_{30}$ compound.

3.3. Refinement and structure analysis

The first structural refinements on the both $La_7Ta_3W_4O_{30}$ and $La_7Nb_3W_7O_{30}$ were analyzed by combining X-rays and neutron diffraction patterns, with a weighing scheme of 50–50%. For the last compound an impurity was detected. The main peaks of this impurity were found with the interatomic distances d: 3.148, 2.666 and 1.732 Å, as shown in Fig. 4. This leads to a pseudo-Scheelite structure with the composition "$La_{0.66}WO_4$" with quadratic cell parameters of $a = 5.33$ Å and $c = 11.70$ Å. The