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Ab-initio structure determination of β-La_2WO_6

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ABSTRACT

The structure of the low-temperature form of β-La_2WO_6 has been determined from laboratory X-ray, neutron time-of-flight and electron diffraction data. This tungstate crystallizes in the non-centrosymmetric orthorhombic space group (no. 19) $P2_12_12_1$, with $Z=8$, $a=7.5196(1)$ Å, $b=10.3476(1)$ Å, $c=12.7944(2)$ Å, and a measured density 7.37(1) g cm^{-3}. The structure consists of tungsten [WO_6] octahedra and tetrahedral [OLa_4]. Tungsten polyhedra are connected such that $[W_2O_{11}]^{10-}$ units are formed.

1. Introduction

Oxides of the formula Ln_2MO_6 [M = Mo or W] have been the subject of several crystallographic studies (see Table 1) and these compounds typically present structural variants based on the fluorite (CaF_2) or scheelite ($CaWO_4$) structural types. β-La_2WO_6, the low-temperature form of La_2WO_6, has been reported previously by Yoshimura and Rouanet [1] and also by Yanoskii and Voronkova [2]; however, no crystallographic information concerning its structure was given.

2. Experimental

Room temperature and the high-temperature X-ray diffraction patterns were collected on a Bragg–Brentano diffractometer (MPD-PRO Panalytical) with Cobalt radiation equipped with a linear detector X'Cellerator and an Anton Paar HTK12 furnace. The high-temperature X-ray diffraction patterns were collected during one night, from [5°–70°, 2θ], for 30, 200, 400, 800 and 1000 °C. Neutron diffraction data were collected on the high-resolution powder diffractometer, HRPD, at the ISIS pulsed neutron source, Rutherford Appleton Laboratory, UK. Data collection was performed on ~15 g of compound at room temperature.

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. The sample was prepared by grinding a small amount of powder in an agate mortar and pestle under dry 1-butanol 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 measurement was performed on a gas picnometer ACCUPIC 1330 (Micromeritics) with helium as gas using approximately 2 g of sample. The temperature of measurement was 24 ± 1 °C.

Transport properties were 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. A 5 mm diameter pellet was used for the measurements with, as electrodes, platinum deposited by sputtering on both faces.

3. Results and discussion

3.1. Synthesis

The compound was prepared with La_2O_3 and WO_3 as starting oxides. Lanthanum oxide powder was dried and decarbonated at 1000 °C overnight prior to use. The oxides were weighed in stochiometric proportions with a 1:1 the molar ration of La_2O_3 and WO_3, and ground together in an agate mortar. The prepared composition was heated up to 1400 °C for one night in an alumina crucible, no particular condition was used in order to cool down the samples. The final compound was white.

The X-ray diffraction pattern was rather similar to those previously study by Yoshimura and Rouanet [1] with the JCPDF reference (00-031-0675). The synthesis of a pure compound is

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rather difficult. As mentioned in the phase diagram studies [3], the different compounds occurring in this phase field do not present any notable solid solution (Fig. 1). Thus, the appearance of the two compounds around the composition La_2WO_6 is common. At lower WO_3 molar fractions, $La_6W_2O_{15}$ (JCPDF 00-031-0674) was observed and for the upper molar fractions $La_{14}W_8O_{45}$ (JCPDF 00-032-0502) was observed. $La_6W_2O_{15}$ presents three crystallographic forms α, β and γ, above 930 °C, between 930 and 620 °C and below 620 °C, respectively. None of the structures of these crystallographic forms have been determined. We are currently working on the high-temperature form α-$La_6W_2O_{15}$, which presents orthorhombic cell parameters. The two other lower-temperature forms present significantly more complex crystallographic structures, and are still unknown. The cell parameters for $La_{14}W_8O_{45}$ have been determined previously by Yanoskii and Voronkova [2]; however, the authors have wrongly attributed these cell parameters to La_2WO_6. We have also confirmed the cell parameters of $La_{14}W_8O_{45}$ using electron diffraction and X-ray diffraction. The real composition of this compound is $La_{18}W_{10}O_{57}$, and details of the structure will be published soon. Thus, we choose a composition slightly in excess of WO_3 (50.1 mol% WO_3), in order to have $La_{14}W_8O_{45}$ and not γ-$La_6W_2O_{15}$ as the secondary phase.

Table 1
Crystallographic parameters (cell and space group) for different compounds of formula Ln_2MO_6 (Ln = lanthanide and M = Mo or W)

Formula	a (Å)	b (Å)	c (Å)	β (°)	Z	Space group
La_2MoO_6 [20]	4.089	4.089	15.99	–	2	$I\bar{4}2\,m$
Nd_2MoO_6 [21]	5.658	5.658	31.586	–	8	$I4_1/acdZ$
Er_2MoO_6 [22]	16.325	10.986	5.331	108.62	8	$C12/c1$
Nd_2WO_6 [23]	5.536	9.231	10.170	–	4	$P2_12_12_1$
Nd_2WO_6 [24]	15.920	11.390	5.508	–	8	$I12/c1$
La_2WO_6	7.520	10.348	12.794		8	$P2_12_12_1$

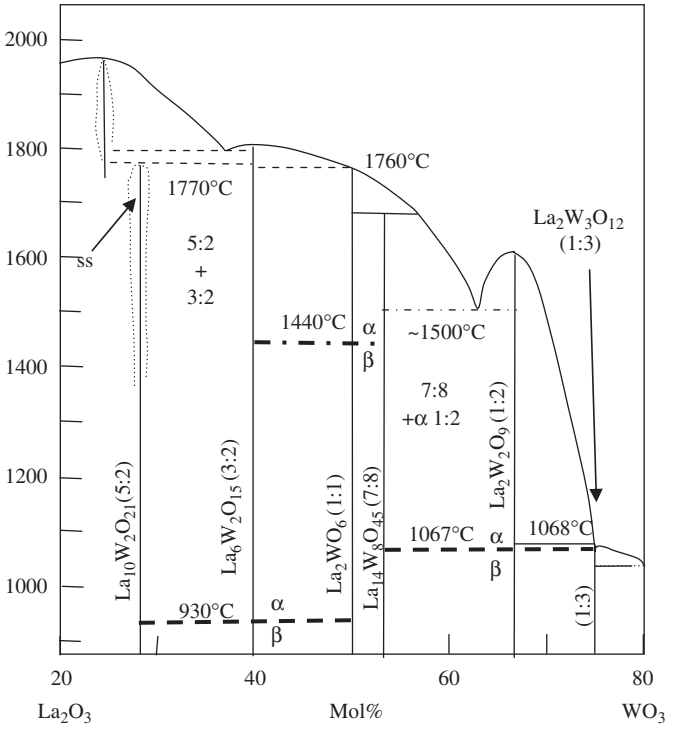

Fig. 1. Phase equilibrium diagram for the system La_2O_3–WO_3 from Ref. [1].

Table 2
Crystallographic parameters of β-La_2WO_6 T.O.F neutron refinement

Atom	x	y	z	U_{iso} (× 100)
La1	0.5666(2)	0.5835(2)	0.4123(2)	0.4(1)
La2	0.7377(2)	0.0552(2)	0.8630(2)	0.6(1)
La3	0.7381(2)	0.5459(2)	0.6736(2)	0.7(1)
La4	0.4787(3)	0.2217(2)	0.5843(2)	2.0(1)
W1	0.5499(4)	0.2294(3)	0.3198(2)	0.2(1)
W2	0.9688(4)	0.1234(3)	0.1279(2)	0.2(1)
O1	0.4738(3)	0.2005(2)	0.9196(2)	0.5(1)
O2	0.0241(3)	0.4384(3)	0.7318(2)	1.4(1)
O3	0.5011(4)	0.2920(3)	0.1813(2)	1.0(1)
O4	0.0309(3)	0.0546(3)	0.4319(2)	0.2(1)
O5	0.0457(3)	0.4572(2)	0.2956(2)	0.6(1)
O6	0.3215(4)	0.3058(3)	0.7526(2)	0.5(1)
O7	0.2502(3)	0.4101(2)	0.9477(2)	0.3(1)
O8	0.3514(4)	0.2475(3)	0.3855(2)	2.0(1)
O9	0.0979(3)	0.0484(3)	0.0201(2)	0.5(1)
O10	−0.1816(4)	−0.3467(3)	0.3000(2)	1.4(1)
O11	0.1732(3)	0.3439(3)	0.5649(2)	0.6(1)
O12	0.1733(3)	0.1161(3)	0.6481(2)	0.5(1)

Bank 1 ($2\theta = 168°$): 1604 reflections, $R_{Bragg} = 7.91\%$, $R_{wp} = 10.6\%$, Bank 2 ($2\theta = 90°$): 638 reflections, $R_{Bragg} = 4.14\%$, $R_{wp} = 6.1\%$.
Space group $P2_12_12_1$ (no. 19), $a = 7.5196(1)$ Å; $b = 10.3476(1)$ Å, $c = 12.7944(2)$ Å, $Z = 8$, Calculated density = 7.44 g cm^{-3}, measured density = 7.37(1) g cm^{-3}.

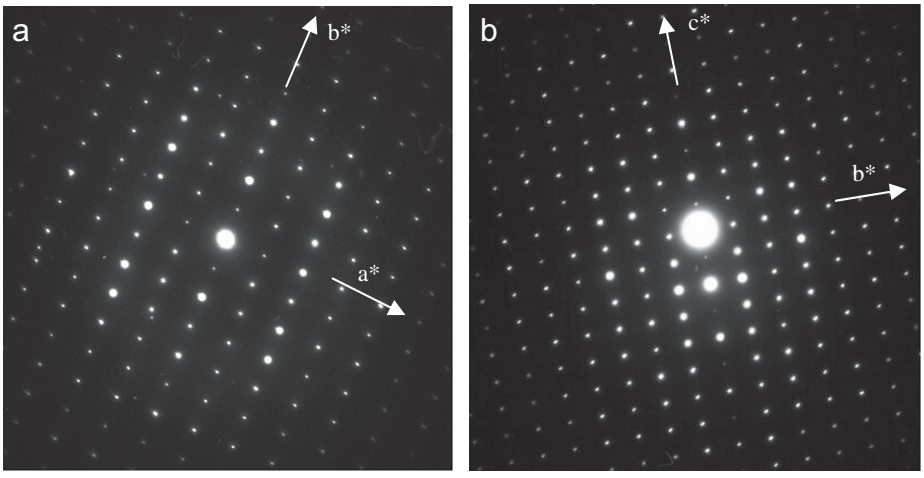

Fig. 2. Electron diffraction patterns of La_2WO_6: (a) along [001]* and (b) [100]*.