



Original Article

Effect of microstructure on electrical and mechanical properties of $\text{La}_{5.4}\text{WO}_{12-8}$ proton conductor



Wendelin Deibert^{a,*}, Vasiliki Stournari^{a,c}, Mariya E. Ivanova^a, Sonia Escolástico^b, José M. Serra^b, Jürgen Malzbender^a, Tilmann Beck^{a,d}, Lorenz Singheiser^a, Olivier Guillon^{a,e}, Wilhelm A. Meulenberg^{a,f}

^a Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research IEK, D-52425 Jülich, Germany

^b Universidad Politécnica de Valencia-Consejo Superior de Investigaciones Científicas, Instituto de Tecnología Química, Av. Naranjos s/n, E-46022 Valencia, Spain

^c Ivoclar Vivadent AG, 9494 Schaan, Liechtenstein

^d University of Kaiserslautern, Institute of Materials Science and Engineering, 67653 Kaiserslautern, Germany

^e Jülich Aachen Research Alliance: JARA-Energy, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany

^f University of Twente, Faculty of Science and Technology, Inorganic Membranes, P.O. Box 217, 7500 AE Enschede, The Netherlands

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ABSTRACT

The relationships between microstructural characteristics and electrical as well as mechanical properties of $\text{La}_{5.4}\text{WO}_{12-8}$ (LWO54) materials were studied. Polycrystalline LWO54 samples revealed identical transport mechanisms regardless of the sample microstructure. The studied samples show predominately proton conductor behaviour below 800 °C and become predominant n-type and oxygen ion conductors above this temperature. The magnitude of the total conductivity is enhanced with larger grain size and lower porosity. Young's modulus decreased by 20% with increasing temperature up to 1000 °C regardless of grain size and atmosphere. Fracture strength was determined via ring-on-ring bending tests, yielding values that strongly depended on microstructural characteristics and homogeneity of the microstructure. Elevated temperature deformation studies revealed that creep is governed by cation diffusion mechanism.

1. Introduction

Hydrogen-related technologies receive growing attention due to the increasing importance of hydrogen as potential environmentally friendly energy carrier of the future with great social impact and economical relevance [1–6]. Therefore, proton conducting oxide ceramics [7–13] are at the emerging focus of materials science and process engineering.

Metal-based alloys [14], including also precious metals such as Pd and Ag [15], yielding H_2 -permeation in the range of few $\text{l}/\text{cm}^2 \text{min}$ at temperatures $T \leq 500$ °C. Microporous inorganic membranes [16,17] are typically used in low temperature H_2 -separation tasks. Dense ceramic membranes as studied in this work are suitable candidates, especially for applications requiring elevated temperatures (600–800 °C). First identified as mixed proton-electronic conductor by Shimura et al. [18], lanthanum tungstate $\text{La}_x\text{WO}_3 + 1.5x$ ($x < 6$, LWO) has been an object of intensive research during the past few years as membrane material for H_2 separation tasks or membrane reactor applications in intermediate to high temperature range [19–29]. In

particular, LWO displays appreciable chemical and (hydro-) thermal stability [24,25], as well as relatively high values of mixed proton-electronic conductivity, after appropriate substitution, in comparison to other ceramic materials [20,23,24]. Such properties are advantageous for application, especially under highly reducing and even sulphur-containing gas environments (e.g. H_2 , H_2O , CO, CO_2 , CH_4 , H_2S , and dust) at elevated temperatures.

In the past years, certain phase purity [21,23,30] and structural issues [31–35] related to this material have been identified and successfully resolved. Lanthanum tungstate was formerly referred to as $\text{La}_6\text{WO}_{12}$, a compound formed in the La_2O_3 - WO_3 system, which was considered stable from room temperature to ~ 2150 °C according to [36] or existing only as a high temperature phase at T higher than ~ 1740 °C according to [37]. In 2001 Diot et al. [38] described the crystal structure as ordered defective fluorite (or disordered pyrochlores) for tungstates with small cations (such as Y and Ho) by a model applicable for $\text{RE}_6\text{WO}_{12}$ (where RE means rare earth). However, lanthanum tungstate with 6-1-12 stoichiometry could not be synthesised as a stable compound as already reported in [21–23] and it finally

* Corresponding author at: Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research, IEK-1, Leo-Brandt-Str., 52425, Jülich, Germany.
E-mail address: w.deibert@fz-juelich.de (W. Deibert).

revealed a much more complex structure for which Diot's model appeared to be unrealistic. Continuous works of Scherb [31] and Fantin et al. [39], independently from Magraso et al. [32] and Erdal et al. [33], have thrown light in particular on the structure of La-tungstate leading to a validated structural model of this complex compound. In addition to the electrical characteristics upon W-substitution explored in literature [23,24], structural characteristics and hydration behaviour of Re and Mo-substituted LWOs with different substitution concentration up to their solubility limits has been furthermore elucidated in a series of recent works [39]. However, any further structure-related details are omitted here, reader can refer to the corresponding works. An important stoichiometry- and structure-related aspect is that the single phase region is relatively narrow (5.3–5.8 in [21]; 5.2–5.5 in [22,23]) and it reveals strong *T*-dependent shift to higher W concentrations reflected by the increased W solubility in the La₂ sites [21,32]. W⁶⁺ partially substituted on La³⁺ cause a decrease in oxygen vacancies concentration and leads to a structure stabilization. In this context, the total electrical conductivity of LWO increases with increasing the La/W ratio as a result of the raised oxygen vacancy concentration, but the stability of main phase suffers. Outside the aforementioned ranges of single phase stability, undesired secondary phases are typically formed e.g. free La₂O₃ at higher La/W ratios [21–23], and La₆W₂O₁₅ phase at lower La/W [22,23,30,40], both having negative impact on LWO material integrity and performance [21–23,30].

Apart from the complexity of composition-structure-defects-transport properties relation, partially elucidated but still requiring massive exploration effort, mechanical properties of this class of materials are scarcely considered. Various studies exist on the mechanical properties of membrane materials focusing mainly on oxygen conducting mixed ion electron conductors [41–46] but very limited contributions have been published on mechanical properties of LWO. An early study by Roa et al. [47] reported material hardness and Young's modulus of LWO materials with La/W ratio in the range of 4.8–6. The main conclusion of their work was the independence of these properties on chemical composition and sintering temperature. Furthermore the densification and variation of the particle size during sintering seems not to vary for different LWO compositions (even though containing secondary phase segregations).

As an attractive candidate for H₂ technology related applications, LWO needs to be manufactured as a membrane, often as an asymmetric structure with a porous substrate and furthermore fabricated in useful geometry and dimensions for later application. Scalable and cost effective methods for fabrication such as tape casting are more and more employed to fabricate LWO membrane components [] and supporting components for LWO membranes [49,50]. However, for developing and optimising the procedure to fabricate defect-free components, in depth knowledge on the influence of the starting powder characteristics on the overall behaviour of ceramic body and furthermore component is required.

Similar to our earlier study on mechanical properties of tape cast porous LWO substrates [26], LWO54 will be employed as a reference composition in the present work. LWO54 stays for La_{28-x}W_{4+x}O_{54+δ}V_{2-δ} material with *x* = 1 (La/W = 5.4) and *δ* = 1.5, resulting in a nominal stoichiometry La₂₇W₅O_{55.5}V_{0.5} (simplified from now on as La_{5.4}W_{1.1}V_{0.1} and abbreviated as LWO54). Considering different compositional and structural aspects already addressed above, it was selected as an optimal compromise between structural stability, sintering parameters and electrical behaviour amongst the range of possible LWOs with different La/W ratio. Ceramic powder with this stoichiometry is also commercially available, which makes it easily accessible for large scale fabrication routes as the tape casting. Therefore, a study has emerged which was carried out addressing LWO54 mechanical and electrical properties as a function of the characteristics of starting ceramic powder and respectively the microstructure of

sintered ceramic body.

2. Experimental

2.1. Powder synthesis and sample preparation

Two different batches of LWO54 powders were used to prepare sintered samples with variable microstructure for further structural, electrical and mechanical investigations in the current work: (1) powder produced via the solid state reaction of mixed oxides and (2) commercially available powder produced by means of the spray pyrolysis with one calcination step at 600 °C in the as delivered state (Cerpotech AS, Norway).

The first LWO54 powder was synthesized following the solid state reaction (SSR) using La₂O₃ and WO₃ as starting oxides (samples labelled LWO54-SSR with a number indicating different batches). For La₂O₃ a preliminary heat treatment step was carried out at 1000 °C for two hours and the powder was weighed at a temperature of 200 °C. The oxides were then mixed in the corresponding stoichiometric ratio and heated to 1500 °C for 12 h for completion of solid state synthesis and phase formation. The resulting powder was ball-milled (24 h) and sieved afterwards.

As a second type of powder, commercially available LWO54 (Cerpotech, Norway) was used (labelled LWO54-SP). This powder was produced by spray pyrolysis and exhibited very fine particle size with a large surface area in as delivered state (labelled as LWO54-SP-1). It was additionally heat treated at 1100 °C to reduce its sintering activity for further processing (labelled LWO54-SP-2). The temperature was correspondingly selected based on the powder sintering behaviour reported elsewhere [26].

From these starting LWO54 powders samples were manufactured by isostatic pressing (pressure 400 MPa, 2 min) and sintered at 1500 °C and dwelling times up to 15 h with heating and cooling ramp of 5 K/min. All microstructural characterisations were performed with the LWO54-SSR and the LWO54-SP-2 powder because they are considered to be most relevant for future manufacturing by sequential tape casting and application.

2.2. Characterization techniques

The chemical composition of the two starting LWO54 powders was monitored by means of the Inductively-Coupled Plasma Optical Emission Spectroscopy (ICP-OES) with a device of Thermo Fisher Scientific (Germany).

The particle size distribution of the starting powders was analysed by means of laser scattering, Horiba LA-950 V2 (Horiba Europe GmbH, Germany).

Additionally, the specific surface area of the powders was determined via the BET method [51] using an AREAmeter II (Ströhlein Instruments, Germany).

Powder X-Ray diffraction (XRD) patterns were recorded in the 2θ range from 10° to 80° using D4 ENDEAVOR diffractometer by Bruker with CuKα radiation. Phase identification was carried out with ICDD PDF2-Database (Release 2004) and X'Pert Highscore Plus (PANalytical). Crystal structures were obtained from the Inorganic Crystal Structure Database (ICSD). XRD analysis was also used to monitor the samples subjected to conductivity measurements for possible structural changes in a post-mortem state. For this purpose, XRD patterns were recorded in the 2θ range from 20 to 90° on a PANalytical CubiX FAST equipment using CuKα radiation.

Microstructural analysis of sintered LWO54 samples were performed either via the SEM using a "Phenom" (FEI) with a backscattered electron detector and acceleration voltage of 5 kV. To analyse the porosity of the sintered LWO54 specimens, multiple SEM images of

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