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A Wet-chemical Method for the Synthesis of In-doped $CaZrO_3$ Ceramic Powders

J. Le,* L. N. van Rij, R. C. van Landschoot and J. Schoonman

Laboratory for Inorganic Chemistry, Faculty of Applied Sciences, Delft University of Technology,
Julianalaan 136, 2628 BL Delft, The Netherlands

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Abstract

Both $CaZr_{0.9}In_{0.1}O_{3-\alpha}$ ceramics and ceramic nano-powders are synthesized starting from a co-precipate formed using a wet-chemical co-precipitation method. The XRD-results confirm that $CaZrO_3$ and $CaIn_2O_4$ phases exist after the co-precipitates are calcined at 1273 K for 3 h in air. The $CaIn_2O_4$ phase disappears after calcining the powder twice at 1823 K for 10 h in air with the formation of the $CaZr_{0.9}In_{0.1}O_{3-\alpha}$ phase. The XRD pattern of the ceramic powders is the same as that of sintered $CaZr_{0.9}In_{0.1}O_{3-\alpha}$ ceramics (1823 K for 10 h in air). Scanning electron microscopy shows that the ceramic powders calcined at 1273 K for 3 h are nano-sized powders. After sintering at 1823 K for 10 h, the grain-size increases dramatically. EDX results indicate that the Ca:Zr:In ratio in the co-precipitates is close to the theoretical value. The ratio of Ca:In decreases with increasing calcining or sintering temperature. © 1999 Published by Elsevier Science Limited. All rights reserved

Keywords: In-doped $CaZrO_3$, powders-chemical preparation, perovskites.

1 Introduction

A variety of acceptor-doped perovskite-type oxides based on $SrCeO_3$, $BaCeO_3$, and $CaZrO_3$ exhibit appreciably high proton conduction in atmospheres containing H_2O at high temperature.[1–3] Therefore, they are promising candidates as an electrolyte in solid-state electrochemical devices such as solid oxide fuel cells, hydrogen pumps, and gas sensors.[4–6] However, there is always a trade-off between high proton conductivity, with a high transference number for protons, and chemical and electrochemical stability under the conditions of a specific application in these proton conducting oxides. It has been known that the acceptor-doped $BaCeO_3$ exhibits the highest proton conductivity, but below approximately 973 K the material is not stable in air with respect to carbonate formation.[7] In contrast, acceptor-doped $CaZrO_3$ is very stable, both thermally and chemically. Although this material exhibits lower proton conductivity than acceptor-doped $BaCeO_3$, it can still be used in low drain applications such as potentiometric sensors.[8]

Traditionally, In-doped $CaZrO_3$ is prepared through a solid-state reaction at high temperatures (1673~1873 K).[9] The main disadvantages of this method are the large structural and compositional inhomogeneities and the high calcining and sintering temperatures.

Recently, In-doped $CaZrO_3$ has been prepared by a hydrothermal synthesis technique.[10] Although the oxide powders prepared by this method exhibit a high purity, a good phase homogeneity and a high degree of crystallinity, it still has a lot of disadvantages.

In this paper, a wet-chemical method has been developed to co-precipitate a nano-powder which is the starting material for the synthesis of In-doped ceramics and ceramic nano-powders.

2 Experimental Procedure

2.1 Synthesis

As precursor materials, indium oxide (99·999% In_2O_3, Aldrich Chem. Co.), calcium carbonate and zirconium oxychloride octahydrate (GR, >99% $ZrOCl_2 \cdot 8H_2O$, E. Merck, Germany) were selected. Di-ammonium oxalate monohydrate (GR, 99·5~101·0% $(NH_4)_2C_2O_4 \cdot H_2O$, E. Merck, Germany) was used as a precipitating agent. The In_2O_3 and

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*To whom correspondence should be addressed.

$CaCO_3$ were dissolved in a hot HCl solution, and $ZrOCl_2{\cdot}8H_2O$ was dissolved in de-ionized water. After these two precursor solutions were completely mixed and diluted with de-ionized water to 0·1 N, a surfactant was added to the mixture to avoid agglomeration of co-precipitated powders.

The co-precipitation was performed using an opposite-dripping technique, that is, the mixture which contained the In^{3+}, Ca^{2+} and Zr^{4+} ions was slowly dripped into an alkaline $(NH_4)_2C_2O_4{\cdot}H_2O$ solution. The di-ammonium oxalate monohydrate was in excess of 25 wt% relatively to the total concentration of $CaCO_3$, In_2O_3, and $ZrOCl_2{\cdot}8H_2O$. The pH value of the precipitating agent was measured using a pH Meter (Schott CG840, Fisher Scientific, Den Bosch, Holland) and controlled at a value of about 9 by continually adding an NH_4OH solution.

Under constant violent stirring, a white co-precipitate was obtained. Subsequently, this co-precipitate was washed several times with de-ionized water and vacuum-filtered until the Cl^--ion concentration of the filtered water became less than 0·01 mol%.

After the washing procedure, the residue was dispersed in absolute ethanol. Replacing water with ethanol can further weaken the agglomeration of the powder in the subsequent drying and calcining process.

The material was first dried at room temperature for 30 min. Further drying was performed at 383 K for 3 h in air. The dried powders, which will be called precursor powders, were calcined for 3 h at 1273 K in air. In order to obtain In-doped $CaZrO_3$ nano-powders, a second calcining step was required and performed at 1823 K for 10 h in air. The heating rate used was $5\,K{\cdot}min^{-1}$.

The oxides calcined at 1273 K for 3 h were pressed into pellets using cold uniaxial pressing ($300\,kg{\cdot}cm^{-2}$). Before pressing the calcined oxides, 8 wt% of a binder (Hoechst wachs C micro binder) was added to the powder. Finally, the pellets were sintered at 1823 K for 10 h (heating rate $5\,K{\cdot}min^{-1}$) in air.

2.2 Characterization

X-ray diffraction (XRD) (Philips, PW1840 diffractor meter) was performed on both powders and the sintered oxides under the following conditions: CuK_α 1·5406A 1·54438A, range $2\theta = 20 \sim 80°$. The microstructure of the powders and the sintered ceramics was investigated by scanning electron microscopy (SEM, JEOL, LV5800), the elements present were identified using energy-dispersive X-ray diffraction (EDX) (Link EXL II).

The density of the specimens was determined from weight and dimension measurements.

3 Results and Discussion

Figure 1 shows the X-ray diffraction pattern of the precursor powders (curve 1). The main crystalline phases are $Zr(C_2O_4)_2{\cdot}4H_2O$, $CaC_2O_4{\cdot}H_2O_7$, and $In(OH)_3$.

A scanning electron micrograph of the precursor powders is given in Fig. 2. As can be seen a nano-sized powder has been formed. EDX results (Table 1) confirm that the ratio of Ca: Zr: In in the precursor powders is uniform and close to the theoretical value of $CaZr_{0{\cdot}9}In_{0{\cdot}1}O_{3\text{-}\alpha}$.

After the precursor powders are calcined for 3 h at 1273 K in air, a ceramic nano-sized powder is obtained with a small particle-size distribution (Fig. 3). The XRD pattern (curve 2 in Fig. 1) reveals that the main crystal phases of the nano-powder are $CaZrO_3$ and $CaIn_2O_4$.

After the ceramic powders are calcined twice at 1823 K for 10 h in air, the $CaIn_2O_4$ phase disappears while the peak positions of the $CaZrO_3$ phase do not change (curve 3 in Fig. 1). This shows that indium has diffused into the $CaZrO_3$ phase.

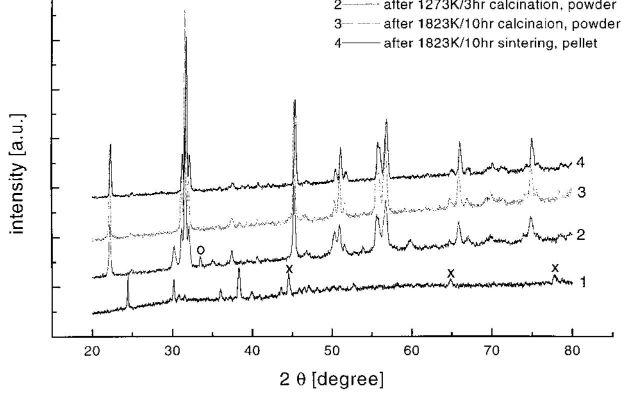

Fig. 1. X-ray diffraction patterns of the precursor powders (1), ceramic powders (2,3) and sintered pellet (4) (o = $CaIn_2O_4$ and x = the A1 sample holder).

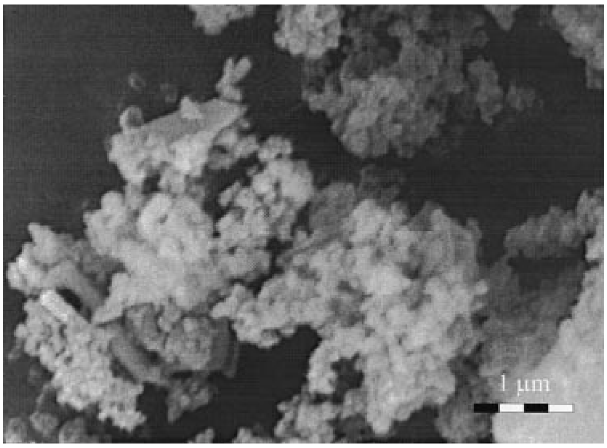

Fig. 2. Scanning electron micrograph of the precursor powders (dried at 383 K/3 h).

Table 1. The element ratio of the precursor powder, the ceramic powders, and the sintered pellets, analysized using EDX

	Precursor powder after 383 K/3 h drying	*Powders after 1273 K/3 h calcination*	*Powders after 1723 K/10 h calcination*	*Powders after 1823 K/10 h calcination*	*Ceramics after 1823 K/10 h sintering*
Ca: Zr	1: 0·82 ± 0·03	1: 0·85 ± 0·03	1: 0·83 ± 0·02	1: 0·84 ± 0·03	1: 0·83 ± 0·02
Ca: In	1: 0·082 ± 0·003	1: 0·098 ± 0·002	1: 0·060 ± 0·002	1: 0·045 ± 0·002	1: 0·042 ± 0·002

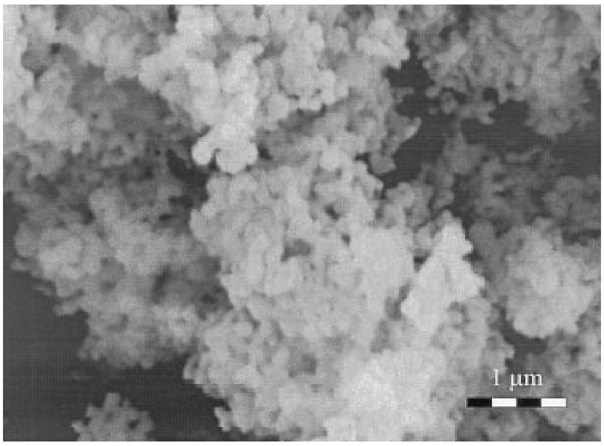

Fig. 3. Scanning electron micrograph of the powder after the first calcining step at 1273 K/ 3 h in air.

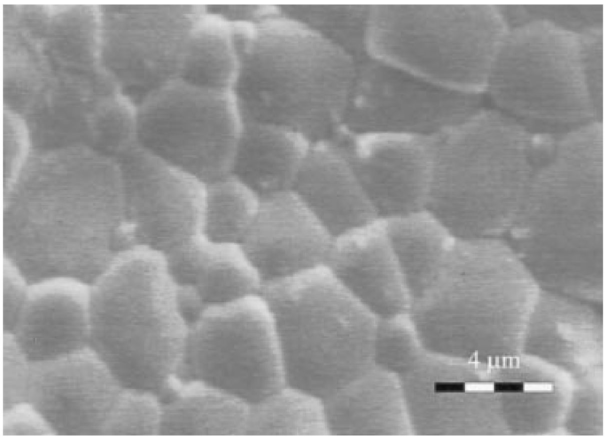

Fig. 4. Scanning electron micrograph of the sintered ceramic (1823 K /10 h sintering).

The $CaZr_{0{\cdot}9}In_{0{\cdot}1}O_{3\text{-}\alpha}$ ceramic powders are brown-yellow and have the same XRD pattern as the sintered $CaZr_{0{\cdot}9}In_{0{\cdot}1}O_{3\text{-}\alpha}$ ceramics (curve 4 in Fig. 1).

The green density of the pressed pellets was 2·70 g cm^{-3}. After sintering at 1823 K for 10 h the density increased to 4·30 g cm^{-3}. The pellets are also brown-yellow. The XRD pattern (curve 4 in Fig. 1) reveals that the main crystal phase of the ceramics is $CaZrO_3$. The $CaIn_2O_4$ phase has disappeared, indicating that indium has diffused into the $CaZrO_3$ phase completely.

The scanning electron micrograph of the sintered ceramic (Fig. 4) shows that the crystal size has increased to about 4–5 μm.

The calcining and sintering temperatures used are still high, but recent results show that a reduction of these temperatures is possible using this co-precipitation technique.

EDX results (Table 1) show that the ratio Ca:Zr in both the ceramic powders and the sintered pellets do not change. The Ca: In ratio, however, decreased after calcining the powder at 1823 K.

4 Conclusions

In-doped $CaZrO_3$ powders have been prepared using a wet-chemical method. XRD analysis shows that after a first calcining step at 1273 K for 3 h in air a $CaZrO_3$ phase co-exists with a $CaIn_2O_4$ phase. The latter phase disappears after a second calcining step at 1873 K for 10 h in air. After pressing the $CaZr_{0{\cdot}9}In_{0{\cdot}}O_{3\text{-}\alpha}$ powder into a pellet, followed by a sintering step at 1873 K for 10 h in air, a $CaZr_{0{\cdot}9}In_{0{\cdot}1}O_{3\text{-}\alpha}$ pellet is obtained with a final density of 4·30 g cm^{-3}.

This is the first report on a wet-chemical synthesis method for In-doped $CaZrO_3$ ceramic powders.

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