

# Effects of the gas flow rate on the ionic conductivity of $\text{CaZr}_{0.95}\text{In}_{0.05}\text{O}_{3-\delta}$ ceramics

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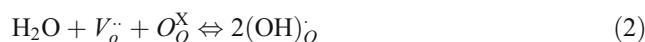
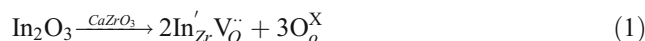
**Abstract** With coarse  $\text{CaCO}_3$ , nano  $\text{ZrO}_2$  and  $\text{In}_2\text{O}_3$  as raw materials, fine  $\text{CaZr}_{0.95}\text{In}_{0.05}\text{O}_{3-\delta}$  powders were synthesized at  $1000^\circ\text{C}$  by an optimized solid-state method. With the powders, ceramics with relative density as high as 98% were successfully fabricated at the temperature as low as  $1400^\circ\text{C}$ . The effects of gas flow rate on the conductivity of the  $\text{CaZr}_{0.95}\text{In}_{0.05}\text{O}_{3-\delta}$  ceramics under wet air conditions were first studied. The results showed that with the increase of temperature, the effects became more and more significant. In order to gain insight into the ion transfer mechanism of the electrolyte, the adsorption and diffusion processes were analyzed. It was suggested that at lower temperature, the diffusion step was the rate-determining step. However, with the increase of the temperature, the adsorption process became the rate-determining step at lower flow rates.

**Keywords**  $\text{CaZr}_{0.95}\text{In}_{0.05}\text{O}_{3-\delta}$  · Proton conductor · Gas flow rate · Adsorption · Diffusion

## 1 Introduction

Humidity and hydrogen sensors become more and more important, principally in controlling systems for industrial processes and human comfort [1, 2]. A wide variety of ceramics, especially those with low-cost, favorable chemical stability and mechanical strength are receiving more attention. Indium doped calcium zirconate ( $\text{CaZrO}_3$ ) is one of the appropriate ceramics to serve as high temperature

humidity and hydrogen sensors, because it is a good proton conductor in steam and hydrogen containing atmosphere at a appropriate temperature range. The transfer mechanism of proton in the ceramics was described as the following [3]: (1) Due to the partial substitution of  $\text{Zr}^{4+}$  with  $\text{In}^{3+}$ , oxygen vacancies are formed as equation (1) indicated. (2) In the steam atmosphere, oxygen vacancies will be filled with  $\text{H}_2\text{O}$  according to equation (2), and the protonic defect is therefore formed.



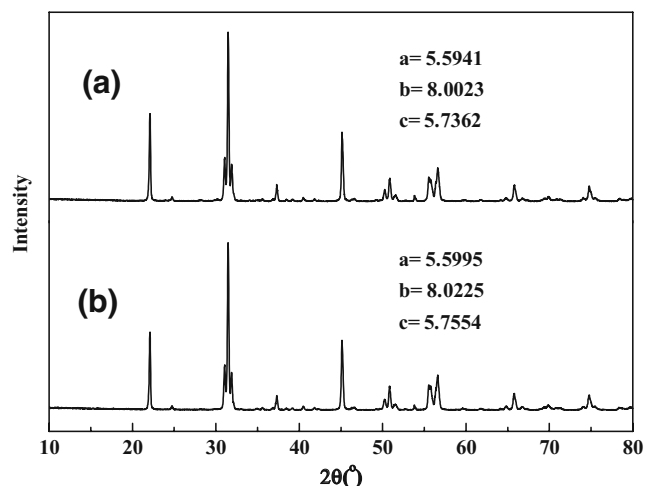
Many factors, such as indium concentration, temperature, influence the conductivity of the In-doped  $\text{CaZrO}_3$  [4, 5]. However, to date, the effects of gas flow rate on its conductivity have not been investigated.

As known, fine grain size is beneficial to the densification of ceramics [6]. In this paper, fine  $\text{CaZr}_{0.95}\text{In}_{0.05}\text{O}_{3-\delta}$  powders were prepared by an optimized solid-state reaction method. Furthermore, the effects of the gas flow rate on the conductivity of  $\text{CaZr}_{0.95}\text{In}_{0.05}\text{O}_{3-\delta}$  were studied.

## 2 Experimental

Stoichiometric amounts of coarse  $\text{CaCO}_3$  (3~5  $\mu\text{m}$ ), nano  $\text{ZrO}_2$  (100 nm) and  $\text{In}_2\text{O}_3$  were first ball-milled for 2 h with ethanol as medium, then dried, pulverised, sieved and synthesized at  $1000^\circ\text{C}$ . The synthesized powders, mixed with 2 wt% of binder agent, were iso-statically pressed under 200 MPa to form pellets and finally sintered at  $1200\sim 1400^\circ\text{C}$  for 10 h to prepare the In-doped  $\text{CaZrO}_3$  ceramics.

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**Fig. 1** XRD patterns of (a)  $\text{CaZrO}_3$  and (b)  $\text{CaZr}_{0.95}\text{In}_{0.05}\text{O}_{3-\delta}$  powders synthesized by the optimized solid-state reaction method

X-ray diffraction (XRD) was carried out (Rigaku RAD-C,  $\text{CuK}\alpha$ ,  $\lambda=1.54056 \text{ \AA}$ ) at room temperature to determine the phase components of the synthesized powders. Field emission scanning electron microscopy (FESEM, JSM-6700) and electron-probe microanalyzer (EPMA, 8705QH2) were conducted to observe the morphology of the powders and the ceramics. The Archimedes' method was employed to test the density of the ceramics with alcohol as medium. Flexure strength of the ceramics at room temperature was determined by the three point bending method (Instron-5500R) with rectangular bars ( $36 \times 4 \times 3 \text{ mm}$ ) at a span length of 30 mm and a crosshead speed of 0.5 mm/min.

For conductivity measurements, platinum was used as block electrode. The measurements were carried out under wet air condition in the temperature range of 600–1000°C by complex impedance on a Solartron 1260 impedance analyzer over the frequency range of 0.1–10<sup>6</sup> Hz.

### 3 Results and discussion

#### 3.1 Synthesis and sintering of $\text{CaZr}_{0.95}\text{In}_{0.05}\text{O}_{3-\delta}$

It was found that fine  $\text{CaZrO}_3$  powders could be obtained by solid-state reaction method via controlling the size of  $\text{ZrO}_2$  reactants in nano level [7]. Therefore, in this paper the size as small as 100 nm was chosen for  $\text{ZrO}_2$  precursors. XRD pattern of the In-doped  $\text{CaZrO}_3$  powder showed in Fig. 1 (b) indicated no impurity peaks other than those of  $\text{CaZr}_{0.95}\text{In}_{0.05}\text{O}_{3-\delta}$ . The increase of the lattice parameters of the In-doped  $\text{CaZrO}_3$  indicated the successful diffusion of indium into zirconium site.

Figure 2 showed the morphology of the precursors and the synthesized In-doped  $\text{CaZrO}_3$  powders. As seen, the particle of the calcined powders [Fig. 2 (b)] was homogeneous with an average particle size of about 110 nm, which was comparable to that of the precursor  $\text{ZrO}_2$  [Fig. 2 (a), 100 nm].

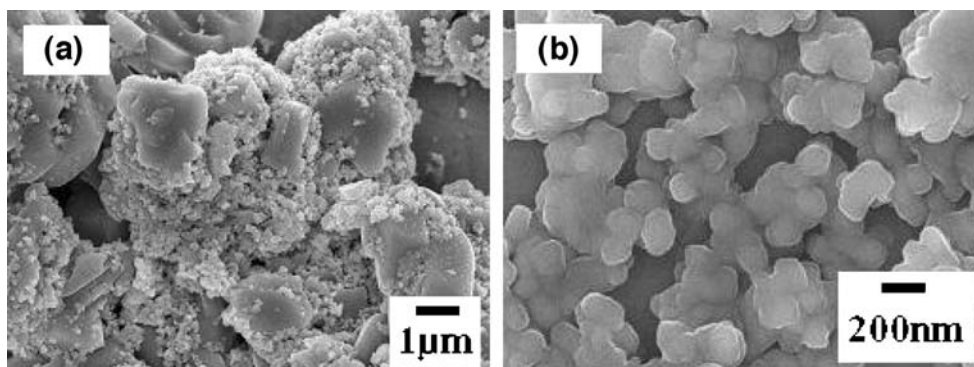
The powders were pressed into pellets and then were sintered. The relative density as high as 98% were obtained for the ceramics sintered at 1400°C, which was nearly 200°C lower than that of the traditional sintering process [8]. The morphologies of the surface and cross section of the ceramics shown in Fig. 3 (a) and (b) verified the high density of the ceramics. The high density of the ceramics obtained in this work could be ascribed to the fine grain size and the high reactivity of its precursor powders.

The bending strength of the ceramics sintered at 1400°C (Fig. 4) was 200 MPa, which was higher than the data previously reported [9]. This could be explained by the Hall-Petch equation,

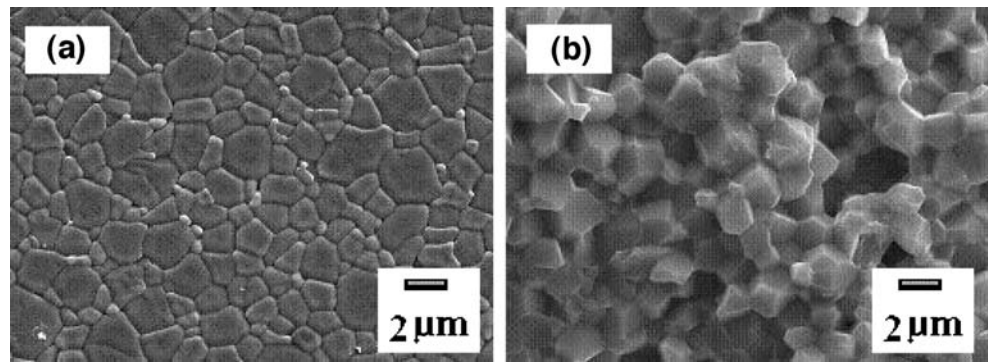
$$\sigma_f = (\sigma_0 + K_1 d^{-1/2}) \exp(-np) \quad (3)$$

where  $\sigma_f$  and  $\sigma_0$  are the mechanical strength with and without porosity, respectively,  $K_1$  and  $n$  are the experimentally constants,  $d$  is the grain diameter and  $p$  is the porosity of the ceramics [10]. The above equation indicated that a smaller  $d$  and lower  $p$  could result in a higher  $\sigma_f$  of the ceramics.

**Fig. 2** SEM images of (a) mixtures of raw materials and (b) synthesized  $\text{CaZr}_{0.95}\text{In}_{0.05}\text{O}_{3-\delta}$  powders



**Fig. 3** EPMA images of (a) the surface and (b) the cross section of  $\text{CaZr}_{0.95}\text{In}_{0.05}\text{O}_{3-\delta}$  ceramic specimen fabricated at  $1400^\circ\text{C}$  for 10 h



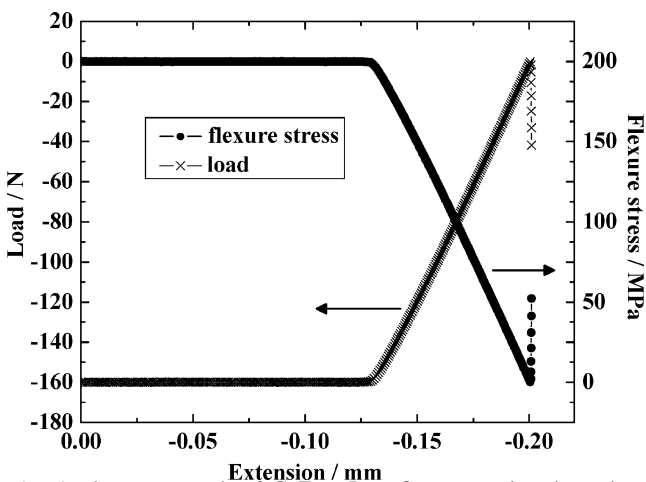
### 3.2 Effect of gas flow rate on the conductivity of $\text{CaZr}_{0.95}\text{In}_{0.05}\text{O}_{3-\delta}$

The conduction mechanism of  $\text{CaZr}_{0.95}\text{In}_{0.05}\text{O}_{3-\delta}$  under wet atmosphere could be proposed as that of the other humidity and hydrogen sensors [11]. It could be described as the following processes: (1) physical adsorption of  $\text{H}_2\text{O}$  on Pt surface; (2) decomposition of  $\text{H}_2\text{O}$  on the  $\text{CaZr}_{0.95}\text{In}_{0.05}\text{O}_{3-\delta}$  surface to form  $\text{OH}^-$  and  $\text{H}^+$  ions; (3) penetration of  $\text{OH}^-$  and  $\text{H}^+$  into the inner part by diffusion; (4) formation of proton defects ( $(\text{OH})_o$ ) by equation (2); (5) transfer of proton defects.

By varying the gas flow rate ( $r$ ), it is possible to identify whether gasdynamics within the electrolyte affects the conductivity performance. Effects of thermodynamic temperature ( $T$ ) and  $r$  on the conductivity ( $\sigma$ ) of  $\text{CaZr}_{0.95}\text{In}_{0.05}\text{O}_{3-\delta}$  were investigated and the results were shown in Fig. 5. Based on the experimental results, the studies were theoretically extended to the operating pressure ( $P$ ) according to the Clapeyron equation,

$$P = \frac{NRT}{V} = \frac{rt/22400}{V}RT \quad (4)$$

where  $V$  is the volume,  $N$  is the number of the moles of gas,  $R$  is the ideal gas constant and  $t$  is the time.

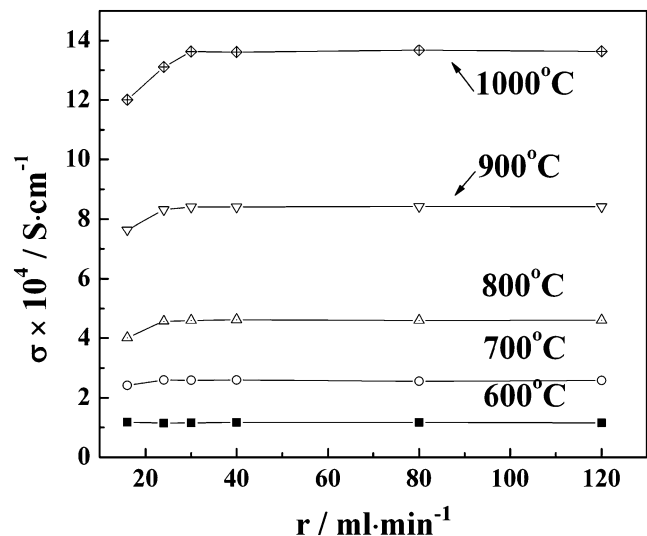


**Fig. 4** Flexure strength of  $\text{CaZr}_{0.95}\text{In}_{0.05}\text{O}_{3-\delta}$  ceramics sintered at  $1400^\circ\text{C}$  for 10 h

According to the Arrhenius equation,

$$\sigma = \sigma_0 \exp(-E_a/RT) \quad (5)$$

(where  $\sigma_0$  is the experimentally derived constant,  $E_a$  is the activation energy),  $\sigma$  was not affected by  $r$ . As Fig. 5 showed,  $\sigma$  kept constant within the whole  $r$  range at  $600^\circ\text{C}$ . However, as the temperatures higher than  $700^\circ\text{C}$ , obvious influences of  $r$  on  $\sigma$  were found. Moreover, the effects became more and more intense with the increase of  $T$ . At  $1000^\circ\text{C}$ ,  $\sigma$  did not reach fixed data until  $r \geq 30$  ml/min. The phenomena could be explained as follows:  $\sigma$  was related not only to the ions diffusion but also to the gas adsorption. While  $T$  was fixed, the diffusion coefficient was remained unchanged, however, the adsorption feature changed with  $P$  and  $r$  [12, 13]. At lower  $T$ , the diffusion coefficient was low and the adsorption quantity was high, therefore, the diffusion process was the rate-determining step, resulting in a constant  $\sigma$  at lower temperature. When  $T$  increased, the diffusion coefficient increased accordingly, but the adsorption capacity, especially the value at lower  $r$ , decreased greatly [12, 13]. Therefore, the adsorbing process became the rate-determining step at lower  $r$  ( $r \leq 30$  ml/min), which would result in the lower  $\sigma$ .



**Fig. 5** Conductivity of  $\text{CaZr}_{0.95}\text{In}_{0.05}\text{O}_{3-\delta}$  ceramics against gas flow rate at different temperatures

#### 4 Conclusions

With fine  $\text{CaZr}_{0.95}\text{In}_{0.05}\text{O}_{3-\delta}$  powders synthesized by the optimized solid-state reaction method, dense ceramic specimen with high mechanical strength was fabricated at the temperature as low as  $1400^\circ\text{C}$ . Effects of the gas flow rate on the conductivity of  $\text{CaZr}_{0.95}\text{In}_{0.05}\text{O}_{3-\delta}$  in wet air were studied. The results demonstrated that at lower temperature, due to the large quantities of adsorbed gas, the diffusion process was the rate-determining step, and there was no effect of gas flow rate on conductivity. However, at higher temperatures, due to the decrease of the quantities of adsorbed gas, the adsorption process became the rate-determining step at lower flow rates, resulting in lower conductivities.

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