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Synthesis and characterization of proton conductive $CaZr_{0.90}In_{0.10}O_{3-\delta}$ by a citric acid complexation method

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ABSTRACT

A citric acid complexation method is applied to synthesize $CaZr_{0.90}In_{0.10}O_{3-\delta}$. TG-DSC, XRD, SEM, linear shrinkage and the complex impedance method are conducted to investigate the physical and protonic conduction properties of $CaZr_{0.90}In_{0.10}O_{3-\delta}$. The results show that the citrate method is a favorable way to produce high purity nano-$CaZr_{0.90}In_{0.10}O_{3-\delta}$ powders suitable for fabricating dense ceramics at lower temperature. In addition, the protonic conduction tests indicate that the total, bulk and grain boundary conductivities of the ceramics are much higher than those of the ceramics fabricated from the powders synthesized by the conventional solid-state reaction method.

1. Introduction

Doped $CaZrO_3$ with perovskite-type structure is well known not only as a high-temperature proton conductor [1,2], but a promising candidate as the electrolyte material for nuclear fusion engineering application, steam electrolyzer, gas sensor and hydrogen analyzer [3–6]. The introduction of In^{3+} is manifested by, what is believed to be, an increase in the ionic conductivity which attains a maximum for 10 mol% In and an increase in mechanical property [7].

The main technique applied to synthesize $CaZrO_3$-based powders is the solid-state reaction method consisting of repeated ball milling and calcinations of the corresponding salts or oxides. This method presents several disadvantages such as long calcining duration, high calcining temperature, and large structural and compositional inhomogeneity. Therefore, it is of considerable significance to apply new routes to the synthesis of $CaZrO_3$-based oxides. For example, an optimized solid-state reaction method was developed to prepare homogeneous $CaZr_{0.90}In_{0.10}O_{3-\delta}$ (δ is the number of oxide ion vacancies per perovskite-type oxide unit cell) at 1000 °C for 6 h [8]. A co-precipitation method was applied to synthesize sub-micron $CaZrO_3$ powders (200 nm) at 1000 °C [9]. A molten salt based method was used to prepare 0.5–1.0 μm $CaZrO_3$ powders at 1050 °C by heating a mixture of $CaCl_2$, Na_2CO_3 and ZrO_2 [10]. High-energy ball milling method was applied to activate reactants and subsequently obtain nanocrystalline $CaZrO_3$ powders by heating the activated samples at 1000 °C for 2 h [11].

We had explored gel precipitation routes in which all of the constituents were mixed in a liquid form as aqueous solution. In the process, the components were mixed thoroughly on the ionic scale and subsequently converted into a solid gel by physical means without segregation. By suitable choice of the gelation process, well-distributed $CaZrO_3$ nano-powders were obtained at 850 °C. It was demonstrated that much lower sintering temperature was required to convert the homogeneous powder to a dense single phase ceramic compared with conventional powder mixing routes [12].

In this work, a citric acid complexation method is applied to synthesize $CaZr_{0.90}In_{0.10}O_{3-\delta}$. TG-DSC, XRD, SEM, linear shrinkage and the complex impedance method are conducted to investigate the physical and protonic conduction properties of $CaZr_{0.90}In_{0.10}O_{3-\delta}$.

2. Experimental

2.1. Sample preparation

The main routes to prepare the $CaZr_{0.9}In_{0.1}O_{3-\delta}$ powders by the citric acid complexation method are shown in Fig. 1. The $Ca(NO_3)_4{\cdot}4H_2O$ (AR), $Zr(NO_3)_4{\cdot}5H_2O$ (AR), $In(NO_3)_3{\cdot}4.5H_2O$ (AR) in stoichiometric proportion are dissolved in deionized water to form a 0.1 M solution of the total metal ions. Then the solution is slowly dropped into a citric acid solution with a mole ratio of citric acid to the total metal ions content of 1:1 to 3:1. The pH value of the mixture is adjusted to 8 with ammonia. The resulting solution is stirred and heated at 60 °C until a viscous liquid is obtained. It is then dried at 60 and 120 °C, respectively, which result in a spongy material. This citrate precursor is burned at 391, 426, 521 and 537 °C to decompose the precursor gradually, then calcined at 600–1000 °C for 2–10 h to yield the oxide powders. The powders are pressed into pellets and finally sintered in air at 1200–1500 °C for 5 h to prepare the ceramic samples.

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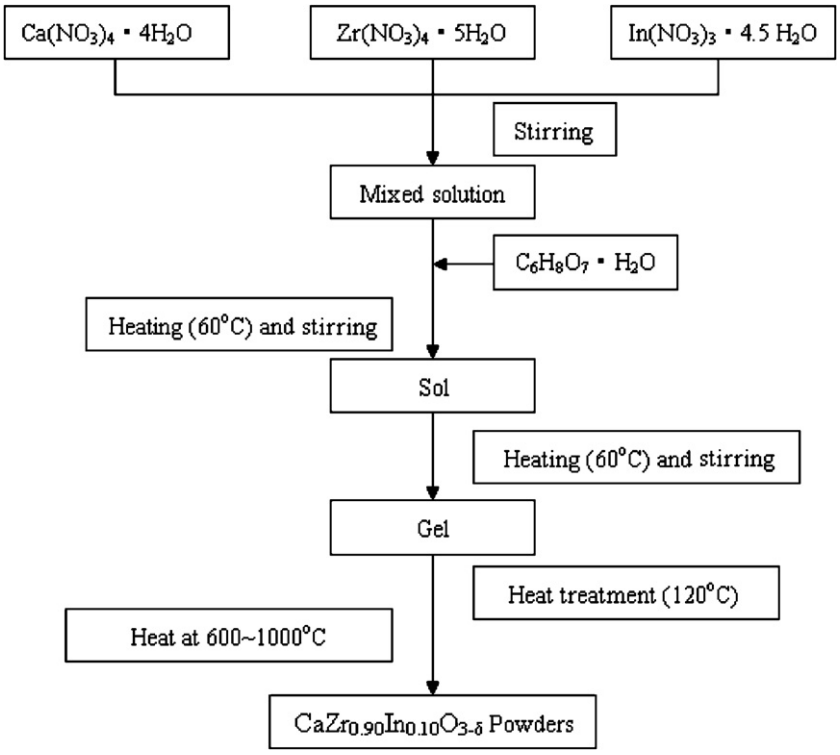

Fig. 1. Flow chart of the synthesis and sintering of $CaZr_{0.9}In_{0.1}O_{3-\delta}$ by the citric acid complexation method.

2.2. Characterization

Thermogravimetric (TG) and differential thermal analysis (DTA) are performed at a heating rate of 5 K min^{-1} from room temperature to 750 °C to study the crystallization process of the $CaZr_{0.9}In_{0.1}O_{3-\delta}$ precursor. X-ray diffraction measurements operated at 40 kV and 100 mA are carried out on a Rigaku RAD-C diffractometer at room temperature to analyze phases of powders and ceramics. Field emission scanning electron microscopy (FESEM JSM-6700) is used to observe the morphology and particle size of the powders and ceramics. The Archimedes' method is employed to test the density of the ceramics with alcohol as the medium. Linear shrinkage measurement is conducted on a DIL 402 PC dilatometer (Netzch, Germany).

For electrical measurement, the sintered $CaZr_{0.9}In_{0.1}O_{3-\delta}$ pellets are polished and covered with platinum ink. Platinum electrodes are formed after firing at 800 °C for 1 h. Impedance spectra are taken under the 5% H_2 + 95% Ar atmosphere ($\log P(O_2) = 10^{-6}$ and $\log P(H_2O) = 10^{-6}$) on a Solartron 1260 impedance analyzer over the frequency range of 0.1 Hz to 1 MHz. The error of temperature control for the test is smaller than 1 °C. Protonic conduction is confirmed primarily by studying the electromotive forces (EMF) of the following gas concentration cell at 600–1000 °C using the specimen ceramics as the electrolyte diaphragm, H_2 (I), Pt|CZIO-10|Pt, H_2 (II). 5% H_2 + 95% Ar, 10% H_2 + 90% Ar and 50% H_2 + 50% Ar are used as H_2 (I) and H_2 (II), respectively.

3. Results and discussion

3.1. Phase analysis

TG-DTA profiles for the $CaZr_{0.9}In_{0.1}O_{3-\delta}$ precursors are shown in Fig. 2. As seen, the thermal decomposition of the precursors consists of several steps. The weight losses from 100 to 350 °C mainly result from the loss of residual water, nitric acid, citric acid, etc. The weight losses in the range from 350 to 600 °C with four corresponding endothermic peaks are ascribed to the decomposition of precursor as the following equations (1)–(4) show [13].

$$2CaZr_{0.9}In_{0.1}O(C_6H_5O_7)_2 \overset{350-405\,^\circ C}{\longrightarrow} Ca_2[Zr_{1.8}In_{0.2}O_2(C_5H_4O_4)_3]CO_3 + CO_2 + 7CO + 4H_2O \quad (1)$$

$$Ca_2[Zr_{1.8}In_{0.2}O_2(C_5H_4O_4)_3]CO_3 + \left[\frac{(27-x)}{2}\right] O_2 \overset{405-470\,^\circ C}{\longrightarrow} Ca_2Zr_{1.8}In_{0.2}O_4(CO_3)_2 + xCO + (14-x)CO_2 + H_2O \quad (2)$$

$$Ca_2Zr_{1.8}In_{0.2}O_4(CO_3)_2 \overset{470-530\,^\circ C}{\longrightarrow} Ca_2Zr_{1.8}In_{0.2}O_5(CO_3) + CO_2 \quad (3)$$

$$Ca_2Zr_{1.8}In_{0.2}O_5(CO_3) \overset{530-600\,^\circ C}{\longrightarrow} 2CaZr_{0.9}In_{0.1}O_{3-\delta} + CO_2 \quad (4)$$

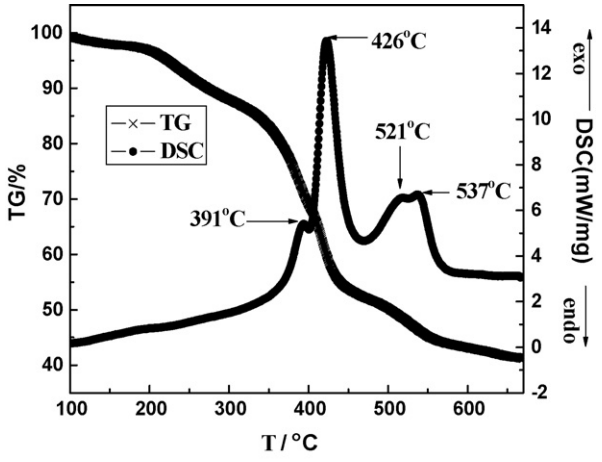

Fig. 2. TG-DSC profiles for the gel precursors of the citrate method.