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Low temperature synthesis of nanocrystalline proton conducting $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ by sol–gel method

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Abstract

Nanoceramic powders of proton conducting $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ (BZY20) have been prepared at low crystallization temperature (below 130 °C) by sol–gel synthesis using all-alkoxide route. Due to a very low crystallization temperature, hydroxyl defects in the lattice crystal are incorporated in-situ during the synthesis process as confirmed by the gradual decrease in the lattice constant from 4.227 to 4.200 on annealing from X-ray diffraction (XRD) analysis, OH vibrations observed in the diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) analysis, and weight loss and heat exchange reaction observed by TG/DTA analysis. The results of XRD have revealed well-crystallized BZY20 peaks of this advanced ceramic material even at low processing temperature. Analysis of FT–Raman spectrum taken at room temperature for the nanocrystalline BZY20 samples prepared at 130 °C using sol–gel processing has revealed an ideal Pm3m cubic crystal symmetry. However, a very slight distortion due to the difference in the B-site sublattice is also observed in the FT–Raman spectrum of the samples upon annealing at higher temperatures. SEM images show the microstructural evolution of the powders from agglomerated nanoscaled crystallites to the nanosized pseudospherical morphology with diameter less than 50 nm. The present low temperature synthesis can be successfully applied to other oxide protonics materials highly doped with protonic defects.

Keywords: Yttrium-doped barium zirconate; Proton conductor; Oxide protonics materials; Nanoceramics; Low temperature synthesis; Sol–gel method

1. Introduction

Solid oxide fuel cell (SOFC) is a promising future technology for a highly efficient, fuel flexible, and clean source of energy. SOFCs using oxide proton conductors as a solid electrolyte, termed as oxide protonics materials, has obtained more interests as compared to traditional SOFC with oxide ion conductors due to its possible low temperature of operation between 400 °C to 700 °C which is a desirable temperature range for both chemical and energy conversion processes [1]. In addition, lowering the operating temperature, in general, can reduce the overall cost. Among other types of acceptor-doped ABO_3 type perovskite structure, Y-doped $BaZrO_3$ has been recently recognized as one of the best proton conducting solid electrolytes due to its high proton conductivity accompanied with high chemical stability. It even exceeds the conductivity of the best oxide ion conductors at temperatures below about 700 °C [2]. Hence, it is a promising material for the realization of this proton conducting SOFCs at intermediate temperature range.

Y-doped $BaZrO_3$ can be synthesized using the classical solid-state reaction methods that usually need high temperatures about 1400–1700 °C and long annealing duration time. This conventional ceramics powder processing can have several drawbacks such as relatively large and varied grain sizes and inhomogeneities in the chemical composition [3,4]. In addition to the difficulty in the processing, due to high volatility of BaO, a possible partial melting at highly doped concentration regions upon annealing at high temperatures, proposed by the present authors, leads to inhomogeneous composition and texture and poor ion conductivity properties. For electroceramic applications such as solid electrolytes in SOFCs, a great demand on the quality of this advanced material for its successful commercial

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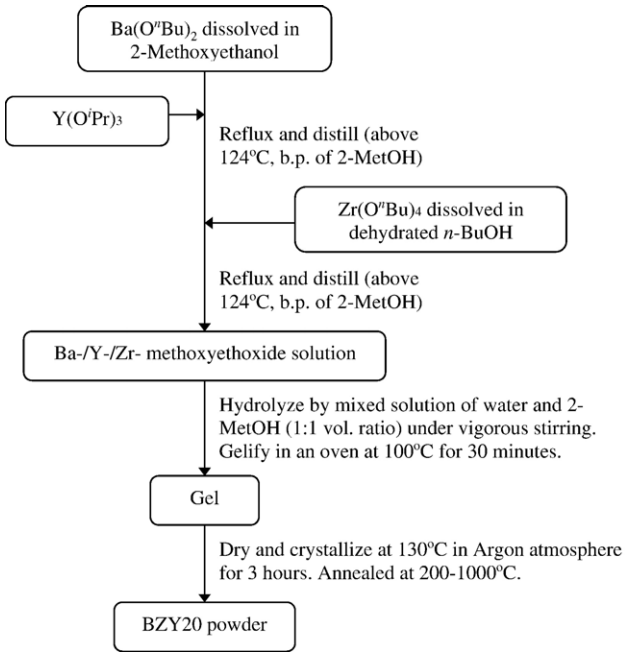

Fig. 1. Flow chart of the sol–gel approach for $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ powder synthesis.

applications has led to a great effort in its processing. In this view, one possible approach to overcome these difficulties is to employ soft chemical process which has the advantages of low synthesis temperatures, shorter processing time, and the possibility of obtaining high purity and ultrafine powders. Essentially, these methods can produce nanocrystalline materials which appear to be a promising approach to combine the superior characteristics of these nanoscaled ceramics with the proton conducting properties of doped perovskites [5]. Moreover, since protonic defects can be incorporated along with the synthetic process, this is an additional advantage over conventional ceramics processing whereby the powder needs to be exposed in a humidified atmosphere after ceramic fabrication in order to fully hydrate and thoroughly incorporate hydroxyl defects into the lattice crystal. Furthermore, one of our targets to develop low temperature processing of oxide protonics materials is to find a novel method to synthesize those materials which are only stable under the coexistence of protonic defects.

There are a very few literatures regarding the powder synthesis of Ln^{3+}-doped $BaZrO_3$ using soft chemical routes (SCR) [3,5,6]. In the case of nondoped $BaZrO_3$ (BZ), a variety of techniques has been employed to synthesize nanocrystalline powder by various types of SCR. These methods can be categorized as (i) sol-precipitation (SP) processes [7–9], (ii) hydrothermal synthesis [7], and (iii) sol–gel method [10,11]. Among these types of processes, the sol–gel method has the advantage of its versatility which can produce a variety of desired products as well as obtaining high purity and ultrafine powders. The molecular level of mixing of the individual components by this method and chemical modification can reduce the diffusion path in the nanometer range to yield crystalline material at lower temperatures [12,13]. In addition, homogeneous distribution of dopant ions can also be easily achieved by this synthetic method [11].

In the present article, we report the low temperature synthesis of proton conducting $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ nanoceramics and the in-situ incorporation of hydroxyl defects using a modified sol–gel approach. The ceramic powder has been fully characterized using powder X-ray diffraction (XRD), field emission scanning electron microscope (FESEM), simultaneous thermogravimetry and differential thermal analysis (TG/DTA), Infrared and Raman Spectroscopy analyses.

2. Experimental

$BaZr_{0.8}Y_{0.2}O_{3-\delta}$ (BZY20) nanocrystalline powders have been prepared via sol–gel all alkoxide route. Barium n-butoxide $Ba(OC_4H_9)_2$, zirconium n-butoxide $Zr(OC_4H_9)_4$, and yttrium isopropoxide $Y(OC_3H_7)_3$ are used as starting materials with 2-methoxyethanol (2-MetOH) as the common solvent. The flowchart for the whole process of BZY20 nanoceramics synthesis is shown in Fig. 1.

2.1. Basic principle of the synthetic approach

In this approach, the principle is to let the starting materials to undergo a complete ligand exchange to form methoxyethoxide ligands and removing other resulting exchange parent alcohols from the starting metal alkoxides. This technique has the advantage of ensuring homogeneous gelation. In addition, the bidentate nature of the methoxyethoxide ligand can tie up vacant coordination sites, lowers hydrolysis rate, and allows the more facile formation of mixed-metal alkoxide complexes [10].

It can be noted that the mixing of the metal alkoxides is tailored to ensure alcoholysis and easier exchange of 2-methoxyethanol with the alkoxide ligands. These resulting alcohols are then removed by distillation. The ligand exchange can be described by the following equation

$$M(OR)_n + nR'OH = M(OR')_n + nROH \quad (1)$$

Notably, the solution has been stable for more than 6 months without precipitation. The high stability is probably due to the bidentate nature of 2-methoxyethanol of which the –OH group forms hydrogen bond with the metals. The 2-methoxyethanol

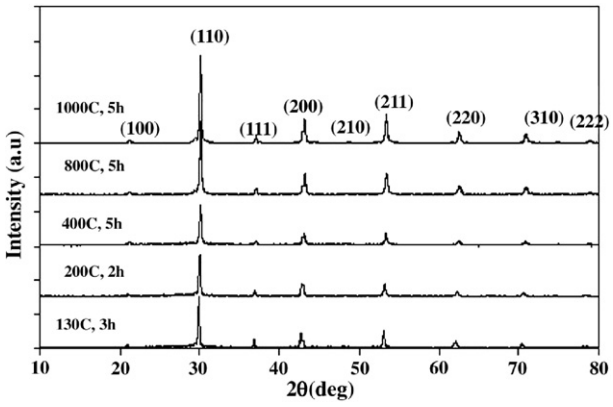

Fig. 2. XRD stack profile of $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ dried and annealed at different temperatures.