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Short communication

Fabrication of yttrium-doped barium zirconate ceramic by high pressure sintering

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A B S T R A C T

A high pressure sintering method was devised to fabricate high density and strength $BaZr_{0.9}Y_{0.1}O_{3-\delta}$ (BZY) ceramic at 0.6 GPa and 1100 °C for the first time. The mechanical properties and electrochemical response of the ceramic in high pressure hydrothermal fluids were tested in a self-designed autoclave. Results shows that the ceramic can be processed into fixed shape, it remains stable and a rapid electrochemical response was observed after exposing to water vapor at 340 °C and 14 MPa for 20 h, which makes the product an excellent candidate electrolyte material for in-situ measurement of H_2 in high pressure hydrothermal fluids.

1. Introduction

Any approach of in-situ measurement of H_2 in seafloor hydrothermal vent fluids faces severe technological constrains due to the extreme environments [1]. It is expected that many of these obstacles can best be overcome with better materials prepared by new and sophisticated methods.

BaZrO3-based oxides are among state-of-the-art electrolyte mate-

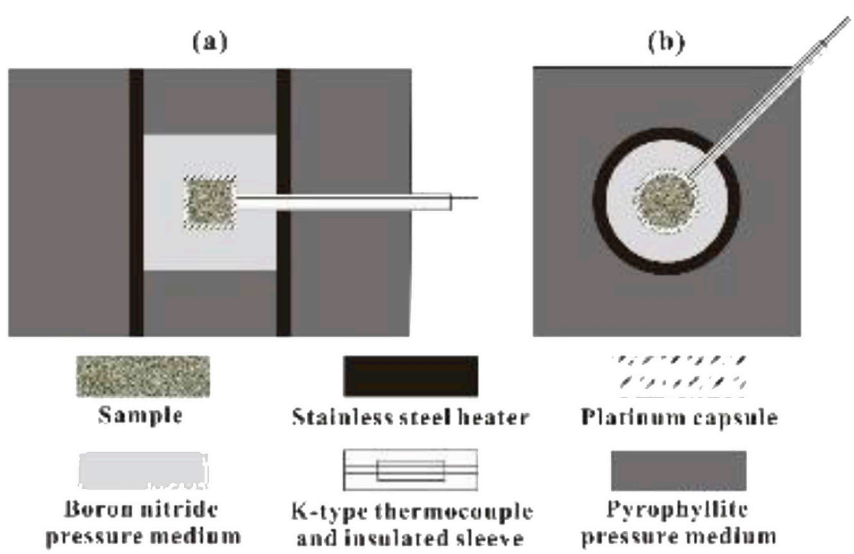

Fig. 1. Sectional view (a) and vertical view (b) of the experimental setup.

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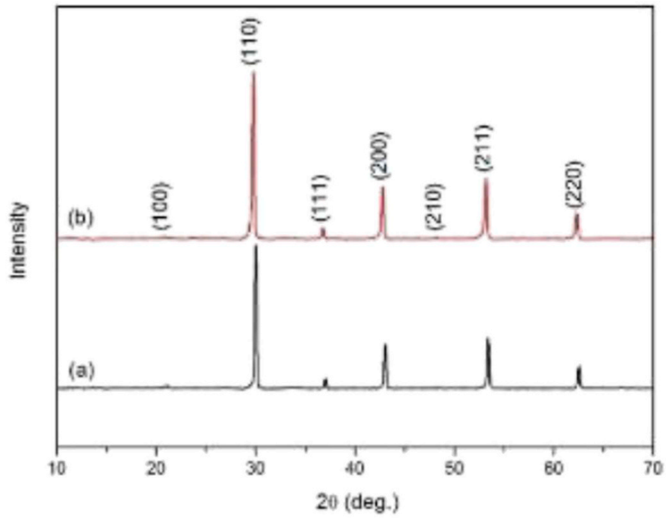

Fig. 2. XRD patterns of (a) BZY powders and (b) BZY ceramic.

rials as they combine good proton conductivity with excellent chemical stability [2,3]. However, the poor sinterability of $BaZrO_3$ limited its actual applications [4], and the mechanical properties of the pressureless-sintered $BaZrO_3$-based ceramic are not good enough to be used in high pressure hydrothermal fluids. In this work, high strength BZY ceramic was fabricated by high pressure sintering at 0.6 GPa and 1100 °C.

2. Materials and methods

$BaCO_3$, ZrO_2 and Y_2O_3 powders were ball-milled and then calcined at 1300 °C for 24 h. The calcined $BaZr_{0.9}Y_{0.1}O_{3-\delta}$ (BZY) powders were pressed into a cylinder compact, the compact was sealed into a platinum capsule and then assembled in accordance with Fig. 1. The high pressure sintering experiment was carried out in the DS-6 × 1400t cubic-anvil high pressure apparatus at 0.6 GPa and 1100 °C for 0.5 h.

The crystalline phases and morphology of the BZY powders and ceramic were analyzed by XRD and SEM. After processing the BZY ceramic into circular truncated cone by a grinder, the platinum electrodes were attached to both ends of the BZY ceramic and subsequently assembled in a tapered bore at the autoclave to create a conical self-energizing sealing structure. One third of the autoclave was filled with deionized water and a concentration cell was formed due to the different hydrogen partial pressures between the inside (water vapor atmospheres) and outside (ambient air atmospheres) of the autoclave.

3. Results and discussion

Fig. 2 shows the XRD patterns of the BZY powders and ceramic. All diffraction peaks match well with the cubic perovskite phase of $BaZrO_3$ (JCPDS card NO. 06-0399), and no additional peaks are detected.

The micrograph of BZY powders is shown in Fig. 3(a), revealing the powders shared the characteristics of small particle size and good dispersity. Fig. 3(b) presents the submicron grains were closely packed together and hardly any pore or crack was observed, which indicates that the well-developed grains are in accord with the high relative density (96%) calculated by Archimedes method. It is evident that the high pressure sintering effectively inhibited the grain growth and increased densification of the BZY ceramic. Elements distribution of the BZY ceramic are shown in Fig. 3(c)-(e), each element was finely dispersed and uniformly distributed.

In order to test the machinability and electrochemical response in high pressure hydrothermal fluids, the BZY columnar was processed into circular truncated cone and then assembled in an autoclave acts as seal and electrolyte. Fig. 4 shows the curves of pressure-time and EMF-time from 300 °C to 340 °C. The BZY ceramic can be processed into fixed shape and the autoclave was hermetically sealed at 14 MPa by using the ceramic as a sealing material, indicating the ceramic has satisfactory mechanical properties. Moreover, the EMF responded rapidly to the change of temperature and pressure, and quickly reached equilibrium after temperature stabilization when BZY sample acting as electrolyte in the concentration cell, which suggests that the sample possesses superior chemical stability and electrochemical response.

4. Conclusions

High density and strength BZY ceramic was prepared by high pressure sintering. Sintering at such a low temperature effectively avoided evaporation of BaO, and pressurizing the sample while heating successfully inhibited the grain growth and increased the densification. Acting as seal and electrolyte shows it possesses superior mechanical properties with rapid electrochemical response. Remarkably, the product is an excellent candidate electrolyte for in-situ measurement of H_2 in high pressure hydrothermal fluids.

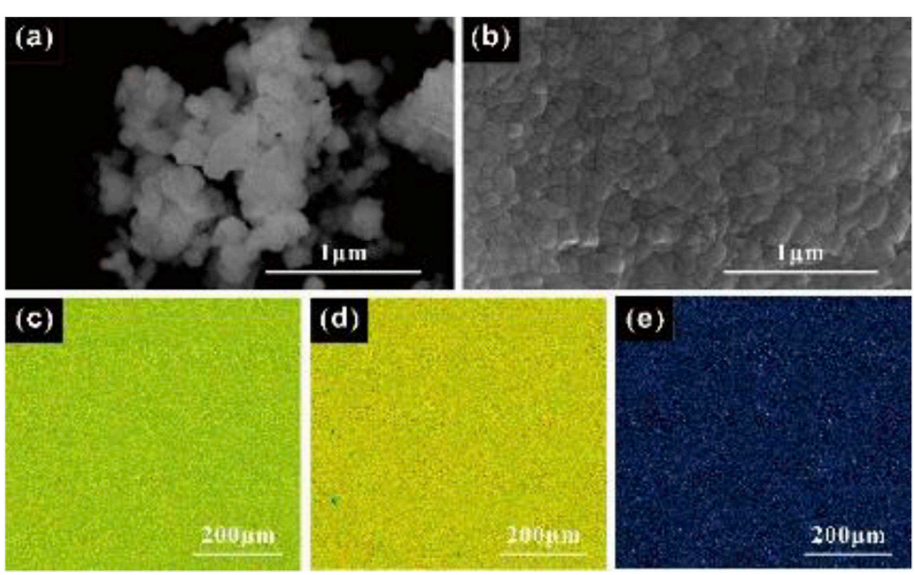

Fig. 3. SEM images of (a) BZY powders, (b) BZY ceramic; Elemental mapping of (c) Ba, (d) Zr, and (e) Y.

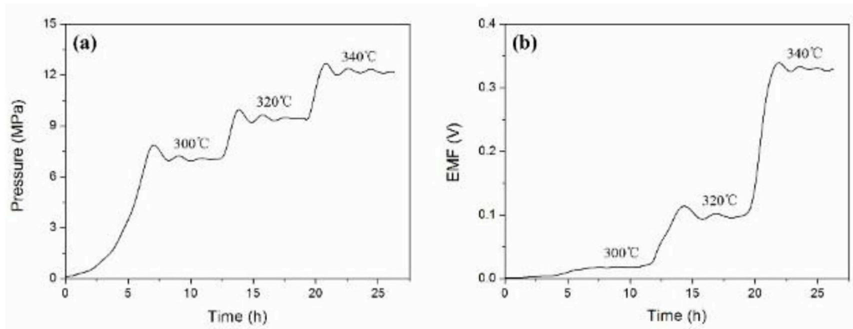

Fig. 4. Pressure-time curve (a) and EMF-time curve (b) when BZY ceramic acts as seal and electrolyte.

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