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# Preparation of scandia stabilized zirconia powder using microwave-hydrothermal method

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**Abstract:** Scandia stabilized zirconia powder (ScSZ) was first synthesized by a microwave-hydrothermal method. The crystalline and aggregated particle sizes were investigated by means of X-ray diffraction (XRD), Raman, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Weakly agglomerated and well crystallized ScSZ powder was prepared by microwave-heating to 150 ºC and 2.5 h. The structure of the ScSZ powder changed from a tetragonal to a cubic phase, and accordingly, the powder conductivity was increased from 90.55 to 120.56 ms/cm by the introduction of the mineralizer solutions (KOH+$K_2CO_3$) during the microwave-hydrothermal processing.

**Keywords:** scandia stabilized zirconia; preparation; microwave-hydrothermal; mineralizer; rare earths

In the past few years, there has been a growing interest in studying the relationship between the electrical behavior and the microstructure of nanosized yttrium-stabilized zirconia (YSZ) and scandia stabilized zirconia (ScSZ), both of which are promising electrolytes of solid oxide fuel cells (SOFCs)[1–4]. Up to now, it has been proved that 10 mol.% $Sc_2O_3$ stabilized zirconia has the highest ionic conductivity among the zirconia-based electrolytes. This could be attributed to the smaller size of $Sc^{3+}$ ions than $Y^{3+}$. The steric blocking effect of $Sc^{3+}$ ions on the movement of oxygen ions is less obvious than that of $Y^{3+}$ ions with larger ionic radius[5,6]. It provides a possibility to lower the operating temperature of the electrochemical devices, leading to much attention to the preparation of nanocrystalline ScSZ[7].

A number of preparation methods including co-precipitation, hydrothermal crystallization, reflux hydrolysis, sol-gel reaction, forced hydrolysis and urea-aided homogeneous precipitation were investigated[8–11]. Among them, hydrothermal crystallization is a more popular method by which finer oxide powder could be readily prepared with less impurity contaminations and low agglomeration degree[12]. However, the hydrothermal method usually requires a very high temperature and a long period of reaction time, resulting in the process being complicated and expensive. A more recent improvement in the hydrothermal method was conducted by Bondioli et al.[13], including the introduction of microwave during the hydrothermal preparation to increase the kinetics of the crystallization by one or two orders of magnitude. According to the recent investigations, microwave heating is an effective way to enhance the crystallinity of prepared powder and decrease the reaction time. Yttria stabilized zirconia powder has been synthesized by microwave-hydrothermal method[14,15]. However, it is not found that ScSZ powder has been synthesized by this method.

In the present paper, crystalline ScSZ was first prepared by the microwave-hydrothermal method. The effects of mineralizers on the crystallization, crystal structure, morphology of powders were also investigated.

## 1 Experimental

### 1.1 Materials and equipment

$ZrOCl_2$ (analytical-reagent grade, Tianyao Chemical Plant, Qingdao, PRC) and $Sc(NO_3)$ (99.5%, Nonferrous Metals and Industry Corp., Zhaoqing, PRC) were used to prepare the stock solutions: the molar ratio of $ZrO_2$ to $Sc_2O_3$ was 9:1, and cation concentration was 1.0 mol/L. The mineralizer solution was prepared with potassium hydroxide (KOH) and potassium carbonate ($K_2CO_3$). Taking the $K_2CO_3$/KOH molar ratio equal to 3, the total (KOH+$K_2CO_3$) concentration was 1.0 mol/L. The ammonia, KOH, $K_2CO_3$ were from Beijing Chemical Factory, PRC. The microwave digestion system (WX-8000)

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was from Preekem Scientific Instruments Co., Ltd., Shanghai, PRC.

### 1.2 Sample preparation

The two stock solutions were mixed and neutralized with 1.0 mol/L ammonia solution to achieve a pH ranging from 9 to 10. The suspensions were filtered and repeatedly washed with distilled water until removal of the chloride ions. Each resulting suspension was treated in a Teflon-lined vessel by using a microwave digestion system in the presence of diluted water. The adopted solid/liquid mass ratio was constant and equal to 1/40. Tests were carried out at 150 ºC for a reaction time of 0.5–2.5 h, then we varied the reaction time from 100 to 190 ºC and fixed the reaction time at 2.5 h. Finally, the suspensions was treated in the presence of mineralizer solutions KOH+ $K_2CO_3$. After microwave hydrothermal treatment, the products were filtered and repeatedly washed with distilled water to remove $K^+$ and dried in a vacuum oven at 85 ºC for 10 h.

### 1.3 Characterization methods

X-ray diffraction patterns for powders were recorded by an X'Pert PRO MPD X-ray diffractometer (PANalytical Co., Ltd., Netherlands) using Cu Kα radiation. The average grain size $d$ was estimated according to the Scherrer equation,

$$d=0.9\lambda/(\beta\cos\theta) \quad (1)$$

Raman spectra was recorded on a Jobin-Yvon U1000 (Academy of Environment Sciences, CAS) scanning double monochromator with a spectrum resolution of 4 $cm^{-1}$ , and the excitation source was an $Ar^+$ ion laser of 532 nm with a power level of 800 mW. Transmission electron microscopy (TEM) observation was performed with a JEM-2000FX (JEOL Co., Ltd., Japan). Scanning electron microscopy (SEM) was carried out using S-4800 (Hitachi High-Tech Co., Ltd., Japan). Powder particle size distribution was carried out by using a Topsizer laser particle size analyzer (Zhuhai OMEC instrument Co., Ltd., PRC). Specific surface area was measured by using ST-8 automated surface area (Qipu Analysis Instrument Institute, PRC). The electricity conductivity was measured by using 4PT Conductivity Testing Manual (Bloom Energy Co., Ltd., USA) after powder was pressed and sintered.

## 2 Results and discussion

### 2.1 XRD analysis

Zirconia has three major crystalline structures, namely monoclinic (m), tetragonal (t) and cubic (c). A tetragonal phase (t″ form) whose axial ratio equal unity is caused by oxygen displacement along the *c*-axis from the ideal fluorite site, is reported to exist in $ZrO_2$-$RE_2O_3$ (RE=Sc, Nd, Sm, Y, Er, Yb) systems[16]. Both t and t″ belong to the same space group of $P4_2/nmc$. Three intermediate ordered phases were determined for $ZrO_2$-$Sc_2O_3$ solid system after being sintered under a high temperature range of 1200–1600 ºC. They are β($Sc_2Zr_7O_{17}$), γ($Sc_2Zr_5O_{13}$) and δ($Sc_4Zr_3O_{12}$)[17]. All three phases have a rhombohedra distortion from the original fluorite structure. It has been proved that the distortion in the phases is caused by the lattice relaxation due to the ordered omission of oxgen ions from the fluorite lattice.

Some samples were prepared at 150 ºC and various reaction time periods from 0.5 to 2.5 h. The XRD results are shown in Fig. 1. From Fig. 1, it is obvious that the diffraction peaks were significantly broadened, indicating the formation of ScSZ nanocrystals when the reaction time was fixed only at 2.0 or 2.5 h under the microwave hydrothermal treatment. The reaction time is much less than that with the conventional hydrothermal methods which usually need 1 to 7 d[18]. The fast reaction should be attributed to that the microwave radiation enhanced the diffusion driving force and made the solution system heat rapidly and uniformly, thus, eliminating the influence of the temperature gradient. As a result, synthesis time required to obtain a good crystallized product was significantly decreased by using microwave hydrothermal method compared to that using a conventional hydrothermal method.

The reflections of the nanocrystals of the sample (Fig. 1) could be basically indexed to be a fluorite cubic phase (c) or t″ formed tetragonal phase. It is difficult to identify the t″ and the cubic phase by XRD analysis due to the peaks broadening resulting from the effect of fine particle size. The diffraction peaks of 111c, 200c, 220c, 311c, 222c, 440c were indexed by using a fluorite cubic phase based on the Standard PDF references of 89-5485. As reaction time is less than 2.0 h, the sample crystallinity was found to be relatively poor, despite that the reflection peaks corresponding to the cubic phase was clear.

Effect of reaction temperature on the crystallisation is shown in Fig. 2(a). All samples were prepared for 2.5 h

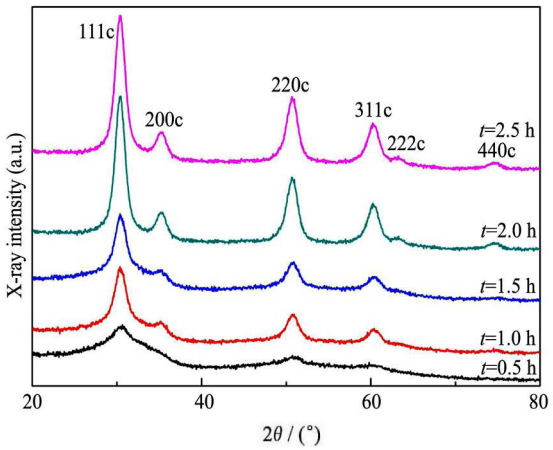


Fig. 1 X-ray diffraction patterns of the ScSZ powders prepared at 150 ºC