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Synthesis and characterization of $Ba(TI_{1-x}ZR_x)O_3$ nanopowders by an aqueous coprecipitation method

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In this study, single phase Ba(Ti_{1-x}Zr_x)O₃ ($0 \le x \le 0.15$) nanopowders have been synthesized successfully by an aqueous coprecipitation method at 85 °C without any further heat treatment. The lattice strain calculated by the Hall-Williamson method indicates that the broadening of the XRD peaks is primarily due to the size of particles not to the lattice strain. The increase of the lattice parameter indicates that Zr ions have entered the lattice and a solid solution was successfully obtained. Furthermore, the particle sizes calculated by the Sherrer formula from the XRD patterns are in agreement with the results of SEM and TEM images. The nanopowders obtained can be used to prepare Ba(Ti_{1-x}Zr_x)O₃ ceramics with a tailored grain size and homogeneous composition, and this is significant to investigate the size effect in Ba(Ti_{1-x}Zr_x)O₃ ceramics and understand the relaxor behavior thoroughly.

Key words: Nanopowders, Ba(Ti_{1-x}Zr_x)O₃, Aqueous co-precipitation.

Introduction

Materials with the perovskite structure have been considered to be promising materials for high dielectric constant capacitors, multilayer ceramic capacitors (MLCC), tunable phase shifters, tunable microwave devices and catalysts [1-2]. Among them, BaTiO₃-based ceramics and thin films have created extensive interest. Substitution of either the A or B sites of the perovskite matrix can modify the phase transition temperature and dielectric and ferroelectric properties. For example, Zr-doped $Ba(Ti_{1-x}Zr_x)O_3$ can modify the phase transition temperature of BaTiO₃, thus modified properties can be obtained. $Ba(Ti_{1-x}Zr_x)O_3$ ceramics and thin films have attracted wide attention for the following reasons: the phase formation mechanism [3], the relaxor behavior [4-5], the piezoelectric properties associated with the high strain level [6], and the dielectric tunability for microwave applications [7-9].

Ba(Ti_{1-x}Zr_x)O₃ exhibits a pinched phase transition when x is about 0.15, with a further increase of x ferroelectric relaxor behavior is observed [8]. The relaxor behavior is caused by the inhomogeneous distribution of Zr ions on Ti sites and mechanical stress in the grains [10]. So it is necessary to prepare Ba(Ti_{1-x}Zr_x)O₃ ceramics with a homogeneous composition. Furthermore, the grain size will affect the relaxor behavior through the large stress caused by the large extent of grain boundaries in fine grain size material. Recently, Ciomaga *et al* [11] reported the relaxor behavior in Ba $(Ti_{1-x}Zr_x)O_3$ for x=0.1 with fine grains. So, in order to investigate the relaxor behavior in Ba $(Ti_{1-x}Zr_x)O_3$ ceramics thoroughly, it is essential to prepare ceramics with a homogeneous composition and a tailored grain size.

Ba(Ti_{1-x}Zr_x)O₃ powders have always been synthesized by a conventional solid-state process which is based on a high temperature reaction between the corresponding oxides and carbonates. The powders obtained are very coarse with an inhomogeneous composition, highly agglomerated and require extensive milling, and are not suitable for preparing ceramics with a homogeneous composition and tailored grain size. This can be realized by a chemical method. In this study, Ba(Ti_{1-x}Zr_x)O₃ (0 ≤×≤0.15) nano powders have been synthesized successfully by an aqueous co-precipitation method at 85 °C without any contamination and the powders can be used to prepare Ba(Ti_{1-x}Zr_x)O₃ ceramics with a tailored composition and a fine grain size.

Experimental Procedure

Commercial TiCl₄, BaCl₂·2H₂O, and ZrOCl₂·8H₂O were used as raw materials without any further treatment. The TiOCl₂ stock solution was prepared by dropping TiCl₄ into ice-cooled de-ionized water slowly with constant stirring. This is because TiCl₄ is very hygroscopic and easily precipitates with water at room temperature. The BaCl₂ solution and ZrOCl₂ solution were mixed with TiOCl₂ stock solution thoroughly for 1h.The molar ratio of Ba/(Zr+Ti) was fixed at 1.1 and the (Zr+Ti) concentration was 0.2 M [12]. The mixed

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solution was then dropped quickly into NaOH solution (15 M) which was heated in an oil bath at 85 °C. The formation of a white gelatinous suspension was observed immediately. The suspension was stirred for 1 h and then the white precipitation was filtered, washed, and dried at 80 °C.

After being dried and de-aggregated, the crystalline phase of the particles was investigated immediately by X-ray powder diffraction (PANalytical Xpert PRO, Netherlands) using Cu K α radiation with 2 θ in the range of 20-80° and a step size of 0.02°.The lattice parameter and lattice strain were calculated from the XRD patterns. The peaks were first stripped K-Alpha2 and the full widths of half-maximum (FWFM) were obtained by profile fitting. Assuming a Gaussian peak profile, the lattice strains were calculated by the Hall-Williamson method using a square relationship written as [13]:

$$(\beta \cos\theta/\lambda)^2 = (0.89/d)^2 + 16\epsilon^2 + (\sin\theta/\lambda)^2$$
(1)

where β is the true FWFM after instrumental collection, θ is the diffraction angle of the center of the peak, λ is the wavelength of the X-rays, d is the particle size and ε the lattice strain. When $(\beta \cos\theta/\lambda)^2$ was fitted linearly versus $(\sin\theta/\lambda)^2$, the lattice strain can be obtained from the slope of the line. The size of the particles was calculated from the broadened XRD peaks using the Sherrer formula:

$$d = 0.89\lambda/(\beta \cos\theta) \tag{2}$$

The average particle size was calculated from the peaks in the range of 20-80°. The morphology of the particles was observed by field emission scanning electron microscopy (FE-SEM, Hitachi S-4800) and transmission electron microscopy (TEM, JEM-2100F).

Results and Discussion

Fig.1 shows the XRD patterns of Ba(Ti_{1-x}Zr_x)O₃ powders precipitated from a solution at a concentration 0.2 M at 85 °C under constant stirring for 1h. The diffraction peaks are indexed to the Ba(Ti_{1-x}Zr_x)O₃ phase with a cubic or pseudo-cubic structure. It is well know that the stable phase of BaTiO₃ is tetragonal and ferroelectric. Although the Zr dopant can decrease the phase transition temperature, it is still above room temperature for Ba(Ti_{0.85}Zr_{0.15})O₃ [9], So the phase for Ba(Ti_{1-x}Zr_x)O₃ ($0 \le x \le 0.15$) should be tetragonal at room temperature. But there is no splitting of (200) peak in the vicinity of 45° in the XRD patterns, which is a characteristic of cubic phase. So the phase should be cubic for Ba(Ti_{1-x}Zr_x)O₃ powders. The disappearance of ferroelectricity and the stabilization of the paraelectric phase at the nanoscale are well reported for BaTiO₃ powders [14]. The mechanisms of stabilization of the paraelectric phase at the nanoscale are very complex,



Fig. 1. The XRD patterns of $Ba(Ti_{1-x}Zr_x)O_3$ nanopowders: (a) x=0, (b) x=0.05, (c) x=0.10 and (d) x=0.15.



Fig. 2. The particle size and lattice parameter of $Ba(Ti_{1-x}Zr_x)O_3$ nanopowders.

such as a surface effect and the lattice strain caused by hydroxyl ions. The stabilization of the paraelectric phase is fatal to the properties of the corresponding ceramics, for example, the dielectric constant is higher for the ferroelectric phase than for the paraelectric phase due to the contribution of domain walls. After being calcined at a higher temperature (about 600 °C), BaTiO₃ nanopowders will bear a phase transition from cubic to tetragonal and ferroelctricity will appear [15], this may be true for Ba(Ti_{1-x}Zr_x)O₃.

The particle sizes calculated by the Sherrer formula are shown in Fig. 2 It can be seen that both the average particle sizes and lattice parameters obtained by the X Pert Highscore Plus software increase with an increase of the Zr concentration. It is well established that the lattice parameter expands with a decrease of the particle size in BaTiO₃ nanopowders, which is due to the variation of the bonding character of Ti ions from covalent to ionic [16]. From the expansion of the lattice parameter, this indicts that Zr ion entered the lattice of BaTiO₃ and a solid solution was successfully obtained. If a solid solution was not formed, the lattice parameter should decline with an increase of particle size from x = 0 to x = 0.15.

It can also be seen from the patterns that the maximum



Fig. 3. Hall-Williamson plot of $Ba(Ti_{0.85}Zr_{0.15})O_3$ nanopowders.

peak intensity decreases with an increase of Zr concentration, which indicates that the crystallizability was improved at higher Zr concentration. The XRD peaks appear significantly broadened, there are two mechanisms caused the broadening of XRD peaks, one is the castalline size effect and the other is lattice strain. To illustrate this, the lattice strain was calculated according to the Hall-Williamson method. Fig. 3 shows the Hall-Williamson plot of Ba(Ti_{0.85}Zr_{0.15})O₃ nanopowders, from the slope of the plot 2.094×10^{-3} was obtained for the lattice strain. The lattice strains are listed in Table 1, although the lattice strain increases with Zr concentration, the overall magnitude of the lattice strain is small (about 2‰). The lattice strain is one times larger than that reported

Table 1. Particle size, lattice parameter and lattice strain of $Ba(Ti_{1-x}Zr_x)O_3$ powders calculated from XRD patterns

	$\mathbf{x} = 0$	x = 0.05	x = 0.10	x = 0.15
Particle size (nm)	21.5	25.6	27.2	28.8
Lattice parameter(Å)	4.0635	4.0708	4.0793	4.0825
Lattice strain($\times 10^{-3}$)	2.069	2.076	2.091	2.094



Fig. 4. FE-SEM images of $Ba(Ti_{1-x}Zr_x)O_3$ nanopowders : (a) x=0, (b) x=0.05,(c) x=0.10 and (d) x=0.15.



Fig. 5. TEM images of Ba(Ti_{0.9}Zr_{0.1})O₃ nanopowders.

by the same calculation method [13, 17], but the particle size is one order finer. From the results of the lattice strain calculations, the broadening of XRD peaks primarily arises from the particle size of the samples.

Fig. 4 shows the corresponding SEM images of Ba(Ti_{1-x}Zr_x)O₃ nanopowders. From the SEM images, the particles are seen to be slightly aggregated with a nearly uniform particle size. It can be seen that the particle size increases with the Zr concentration, which is in agreement with the XRD results. A TEM image of Ba(Ti_{0.9}Zr_{0.1})O₃ nanopowders is shown in Fig. 5, the particle size obtained from the TEM is also in agreement with the XRD and SEM results. Ba(Ti_{1.x}Zr_x)O₃ ceramics with a tailored grain size and homogeneous composition can be realized using the powders obtained in the present study, and this is significant to investigate the size effect in Ba(Ti_{1.x}Zr_x)O₃ ceramics and understand the relaxor behavior thoroughly.

Conclusions

Single phase Ba(Ti_{1-x}Zr_x)O₃ ($0 \le x \le 0.15$) nanopowders have been synthesized successfully by an aqueous coprecipitation method at 85 °C. The broadening of the XRD peaks primarily arises from the particle size of the samples not from the lattice strain. The expansion of the lattice indicates that Zr ions enter the lattice and a solid solution was successfully obtained. The particle sizes calculated from XRD are in agreement with the SEM and TEM images. The nanopowders obtained can be used to prepare Ba(Ti_{1-x}Zr_x)O₃ ceramics with tailored grain sizes and properties, and this is significant to investigate the size effect in Ba(Ti_{1-x}Zr_x)O₃ ceramics and understood the relaxor behavior thoroughly.

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