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Aqueous Co-precipitated spherical shape $PbZrO_3$ nanopowders: Perovskite phase formation

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Abstract

The perovskite phase formation of nanocrystalline powder of lead zirconate ($PbZrO_3$, PZ) was investigated. The structure, phase formation and morphology of PZ powders were characterized using the X-ray diffraction technique (XRD), Fourier transform infrared (FT-IR) spectroscopy, Raman spectroscopy, transmission electron microscope (TEM) and differential scanning calorimetry (DSC). Tetragonal zirconia (t-ZrO_2) phase was found as an intermediate phase during the calcinations process, followed by the crystallization of the orthorhombic PZ phase. The change in relative amount of the residual t-ZrO_2 phase as a function of calcination temperature was estimated from the relative intensities of selected Raman peaks. From a TEM photograph, the $PbZrO_3$ powder was found to be spherical in shape with uniform nanosized features. The average particle size for the calcined powders was about 10.44 ± 1.21 nm.

Keywords: Antiferroelectric; $PbZrO_3$; Precipitation method

1. Introduction

There has been increasing interest over the past few years in the synthesis of ferroelectric nanocrystals because of their scientific importance and widespread application in the electronics industry [1]. Lead zirconate ($PbZrO_3$, PZ) is an antiferroelectric ceramic used in high energy density capacitors and large strain actuators, due to the behavior of electric field-induced antiferroelectric to ferroelectric phase transformation [2]. The traditional solid state reaction route, in which an appropriate amount of zirconium and lead oxide is mixed and fired together, can be a simple technique to synthesize lead zirconate. However, the volatility of PbO is a major problem in this method, and the preparation of $PbZrO_3$ requires a high temperature [2]. It is well known that the synthesis of multicationic oxides by traditional solid-state reaction suffers from several drawbacks. Therefore, various techniques have been developed, with many investigations focusing on wet chemical methods. Wet-chemical or chemical solution methods are also used to produce more homogeneous, finer particle size and lower impurity level powders than those produced by the solid state reaction method [1], and they can be excellent for the synthesis of pure and highly reactive multicomponent powders. On the other hand, it is also possible to synthesize perovskite PZ from aqueous solution by the co-precipitation method. The formation from $Pb(NO_3)_2$, $ZrOCl_2 \cdot 8H_2O$ and KOH precursor mixture is not available in the literature.

This work reports on the perovskite phase formation of $PbZrO_3$ synthesized by the aqueous co-precipitation method. The phase formation and mechanism of the powders calcined in various conditions are studied and discussed in this paper.

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2. Experiment

$Pb(NO_3)_2$ (purity 99.5%) and $ZrOCl_2 \cdot 8H_2O$ (purity 99.5%) were used as starting materials. 15 mol/L of KOH was used as a mineralizer. An aqueous solution of 1.0 mol/L lead nitrate was prepared using deionized water. The required amount of $ZrOCl_2 \cdot 8H_2O$ was dissolved in the 15.0 mol/L of KOH with continuous stirring to form a suspension. $Pb(NO_3)_2$ was added drop-wise into the suspension of $ZrOCl_2 \cdot 8H_2O$ under vigorous stirring. Finally, the white precipitate was formed. The recovered precipitate was separated by centrifugal filtration (3000 rpm) and washed with deionized water before drying in air at 90 °C overnight. The final precipitate was calcined at various temperatures (300–900 °C) in air, followed by phase identification measurement using an X-ray diffractrometer (Bruker D8 Advance diffractrometer). IR spectra were measured by an FT-IR spectrometer (Perkin–Elmer, Spectrum GX spectrometer). Visible laser light was used for Raman measurements (DXR Raman microscope, Thermo Scientific). The powder morphology and size characterization were performed by transmission electron microscope (TEM, Philips TECNAI 20). The phase transitions also were measured by a differential scanning calorimeter (DSC 2920, TA Instrument).

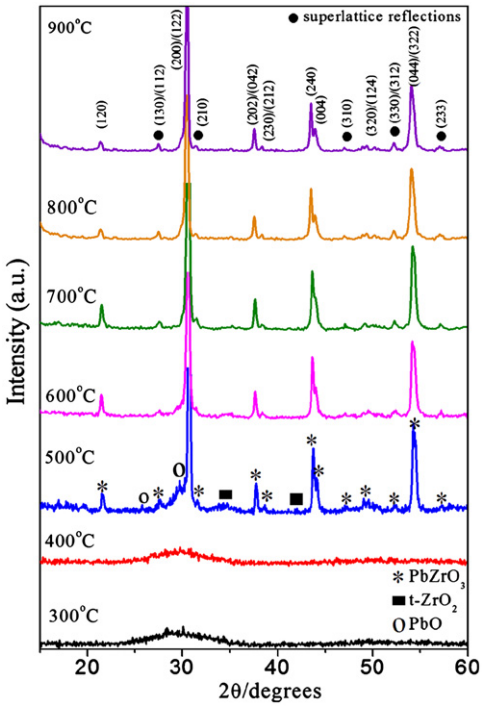

Fig. 1. XRD pattern of $PbZrO_3$ powder at various calcination temperatures from 300 °C to 900 °C.

3. Results and discussion

The X-ray diffraction pattern of PZ powder, during 4 h of calcination at temperatures ranging from 300 to 900 °C, is shown in Fig. 1. Powders at 300 and 400 °C showed broad humps centered at 28° of 2-theta degrees, thus signifying the presence of an amorphous hydrated zirconia phase [3] with no evidence of a perovskite PZ phase. When the calcination temperature increased to 500–800 °C, the perovskite-type PZ phase (indicated by a star) appeared, thus revealing the presence of a pyrochlore phase. The small intensity reflection peaks at around 25.14° and 29.08° of 2-theta degrees (indicated by an open circle) could be assigned to the PbO phase, which agreed well with the standard data (JCPDS: 77-1971). The small peaks at around 34.50° and 50.13°of 2-theta degrees (indicated by a solid square) corresponded to the ZrO_2 phase, which was consistent with the standard data (JCPDS: 79-1769) for tetragonal structure. Although XRD is not sensitive enough to distinguish the tetragonal zirconia (t-ZrO_2) phase in small amounts, Raman spectroscopy [see Fig. 2(b)] could identify it. The precursors were transformed into $PbZrO_3$ phase only when the calcination temperature increased to 900 °C. It can be seen that the perovskite-type PZ phase was presented clearly in the X-ray diffraction pattern at 900 °C, as no diffraction from PbO, ZrO_2 and the other phase was detected.

The XRD data show that 1/4 (*h k l*) superlattice reflection peak (indicated by solid circles) and splitting peaks (2 4 0) are observed clearly for powder calcined at 500–900 °C, indicating that the major phase in these powders had an orthorhombic symmetry. The reflections of $PbZrO_3$ were consistent with JCPDS file no. 20-0608. The cell parameters were calculated by the Rietveld method using REX software, and found to be $a=5.875(3)$ Å, $b=11.718(1)$ Å and $c=8.310(3)$ Å. The values of cell parameters were close to (within 0.20) that reported for $PbZrO_3$ in standard data (JCPDS: 20-0608). From the reflection peak, the average crystalline size of $PbZrO_3$ powder was 9.03 ± 0.2 nm, calculated from Full Width Half Maximum (FWHM) using the Scherrer equation [4].

The FT-IR spectra are shown in Fig. 2(a). For all powders, the intensive broad band of around 3457 cm^{-1} and less intensive band at 1630 cm^{-1} can be attributed to the asymmetric stretching and bending vibrations of the O–H bond, respectively [3]. It is noteworthy that vibrations of around 3457 and 1630 cm^{-1} were found for powders calcined at 300–900 °C, despite the powder passing through the calcination process. Two absorption bands in the vicinity of 1347 cm^{-1} and 1570 cm^{-1} can be attributed to the symmetric and asymmetric vibrations of the NO_3^- group, which is due to the existence of a small amount of nitrate from the precursor. The peak of around 417 cm^{-1}, shoulder at 915 cm^{-1} and strong absorption peak at 530 cm^{-1}, can be assigned to intrinsic stretching vibration of metal-oxygen of Zr–O modes [3,4], which emerged when the calcination temperature increased to 500 °C, and intensity increased with increasing calcination temperature. No bands associated with vibrations involving mainly lead ions were observed in the mid-infrared spectral region.

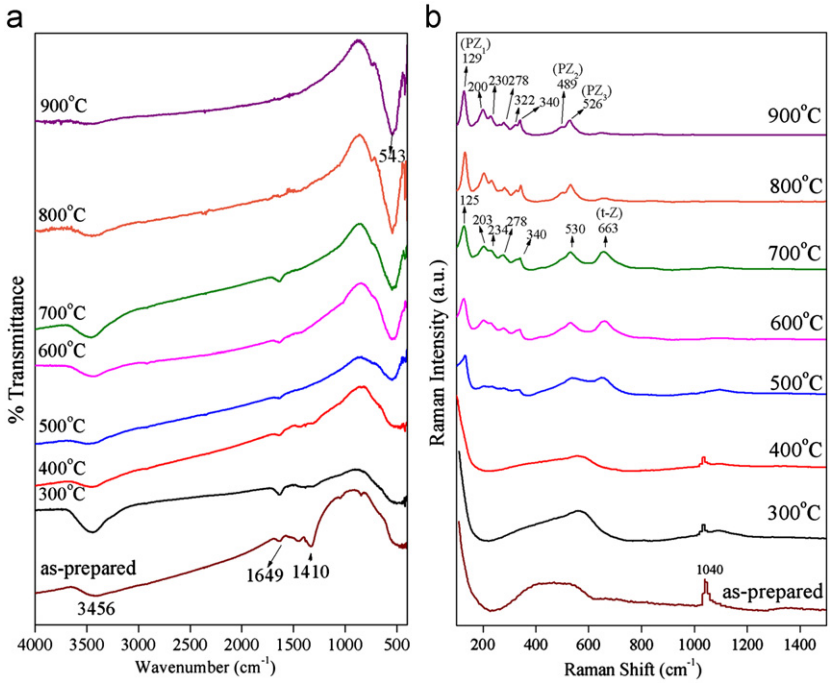

Fig. 2. (a) IR spectra of $PbZrO_3$ powder and (b) Raman spectra for as-prepared powders and powders calcined in the range from 300 °C to 900 °C.

These results suggest that the perovskite phase can be obtained at 500 °C, while no reaction is initiated from the as-prepared and calcined powder at temperatures lower than 500 °C. The result by Raman spectrum is shown in Fig. 2(b). The presence of a band at 1046 cm^{-1}, which relates to symmetric stretching of NO_3^- in as-prepared powder, can be assigned to the residual nitrate staying in the powder. Intensity of the peak at 1046 cm^{-1} decreased with increasing calcination temperature and disappeared when the temperature rose to 500 °C, which corresponded to the FT-IR result. Regarding powder calcined at 500 °C or higher temperature, the presence of a peak at 133 cm^{-1} related to the Pb lattice soft mode. A peak of around 201 and 209 cm^{-1} could be related to bending motions of the Zr–O mode; to a peak in the range from 300 to 450 cm^{-1} and 490 to 600 cm^{-1} that could be attributed to the Zr–O_3 torsionnal modes and Zr–O stretching motions, respectively. These peaks were a typical Raman spectrum of the PZ phase [5], indicating that the PZ phase was started at 500 °C, and in agreement with the XRD results. Intensity of the PZ peak increased with increasing calcination temperature. In addition, conclusive evidence of the tetragonal zirconia (t-ZrO_2) intermediate phase was present at 652 cm^{-1} in the Raman spectrum [6]. The t-ZrO_2 phase began presenting at 500 °C before intensity of this peak decreased with increasing calcination temperature until it disappeared at 900 °C; a temperature that could change the t-ZrO_2 intermediate phase to the $PbZrO_3$ phase.

According to the formation mechanism, this work could propose perovskite phase formation of lead zirconate ($PbZrO_3$) in the following steps.

For as-prepared powders and powders at $t \leq 400$ °C

$$Pb(NO_3)_{2(aq)} + ZrOCl_2 \cdot 8H_2O_{(aq)} + 4KOH_{(aq)} \rightarrow Pb(OH)_{2(s)} + Zr(OH)_{4(s)} + 2KNO_{3(aq)} + 2KCl_{(aq)} + 7H_2O_{(l)} \quad (1)$$

At 400 °C < t < 500 °C

$$Pb(OH)_{2(s)} + Zr(OH)_{4(s)} \rightarrow PbO_{(s)} + t\text{-}ZrO_{2(s)} + 3H_2O_{(g)} \quad (2)$$

At 500 °C < t < 800 °C

$$PbO_{(s)} + t\text{-}ZrO_{2(s)} \rightarrow (1-x-y)PbZrO_{3(s)} + xPbO_{(s)} + yt\text{-}ZrO_{2(s)} \quad (3)$$

At ≥ 900 °C

$$(1-x-y)PbZrO_{3(s)} + xPbO_{(s)} + yt\text{-}ZrO_{2(s)} \rightarrow PbZrO_{3(s)} \quad (4)$$

The amorphous precipitate of lead hydroxide ($Pb(OH)_2$) and zirconium hydroxides ($Zr(OH)_4$) for as-prepared powders and powders calcined at a temperature less than 400 °C was formed according to reaction (1), which indicated that amorphous hydroxide is suitable for forming in an early state. Then, when the temperature was in the range from > 400 to < 500 °C, the $Pb(OH)_2$ was changed to the PbO phase, while $Zr(OH)_4$was changed to the intermediate phase of the tetragonal zirconia (t-ZrO_2) phase, according to the reaction (2). The PbO and t-ZrO_2 were reacted to form $PbZrO_3$ subsequently when the calcination temperature was between 500 °C and 800 °C. However, a small amount of PbO and t-ZrO_2 phase was still present at these temperatures, according to the

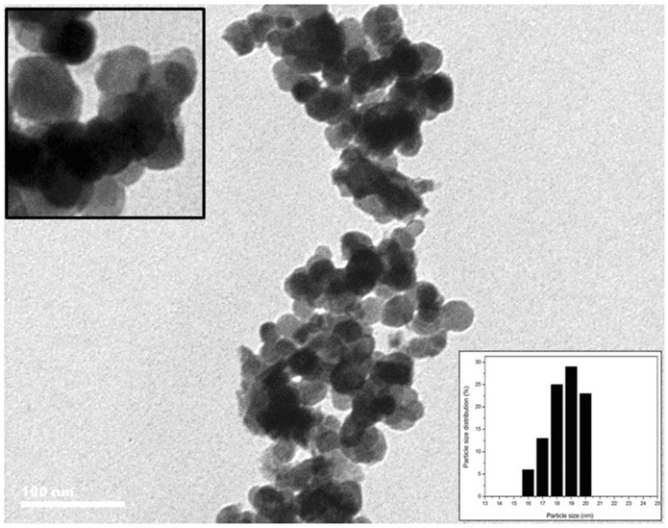

Fig. 3. TEM photograph of $PbZrO_3$ nanoparticles calcined for 4 h at 900 °C.

reaction (3). The amount of t-ZrO_2 phase decreased when the temperature was increased, as revealed by Raman spectroscopy. This suggested that the perovskite, $PbZrO_3$, was formed at a temperature between 500 °C and 800 °C, but not completely. Finally, the precursor was transformed completely into a single phase, with the orthorhombic structure, $PbZrO_3$,and t-ZrO_2 intermediate phase disappearing after 4 h calcination at 900 °C, according to the reaction (4). It is noteworthy that the t-ZrO_2 phase in powders calcined at 500–800 °C was not detected by the XRD method, probably because of its small amount, and the intensity of the t-ZrO_2 phase being very low when compared with that of perovskite phase. Raman spectroscopy can be used to distinguish the crystal phases of small particle size zirconium solid solutions, since vibrational modes are dependent strongly on structure and composition [5,6]. Transmission electron microscopy also was employed for the study of morphology. The morphology of PZ powder calcined for 4 h at 900 °C is shown in Fig. 3. The powder was found to be only spherical in shape, with uniform features. No other phase or pyrochlore phases were found, which suggested that this powder was homogeneous. The powder consisted of primary particles that were measured in nanometers. The average particle size, which can be estimated from TEM photographs, was found to be 10.44 ± 1.21 nm.

The change in enthalpy (ΔH), as measured by differential scanning calorimetry of a sintered $PbZrO_3$ sample and $PbZrO_3$ nanocrystal, is shown in Fig. 4. An endothermic peak is evident clearly at around 231.14 °C for a micrometer size of $PbZrO_3$, with a change in enthalpy of 4.0 J/g. It is well known that the phase transition of PZ crystal is a first-order phase transition, due to the volume change associated with the transformation of the orthorhombic to cubic structure at the curie temperature of 230 °C, whereas the nanocrystal $PbZrO_3$ showed no transition.

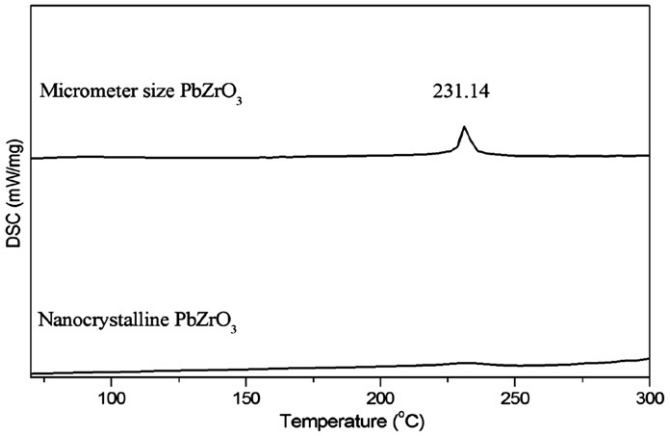

Fig. 4. DSC curves from $PbZrO_3$ nanocrystals calcined for 4 h at 900 °C, and the micrometer size of $PbZrO_3$ ceramic.

It is interesting to note that the effect of size influences the ΔH value and Curie temperature. The absence of exothermic peak at around 230 °C may lead to suggest that the peak value of enthalpy (ΔH) became weaker, and the enthalpy (ΔH) anomaly gradually broader, with decreasing micrometers to nanometers in size. Also, the Curie temperature may be shifted lower or higher than the temperature in this range (100–300 °C), which corresponds to the report from Xiao et al. [7]. On the other hand, the endothermic transition peak could not be detected because of the lattice hydroxyl ion (OH^-) effect on the perovskite structure, which corresponds to the research on $BaTiO_3$ [8]. Badheka et al. [8] reported no change in phase transition for $BaTiO_3$ nanoparticles, but a change occurs in the phase transition when the powder is treated with DMF for 24 h at 170 °C. They reported that the hydroxyl ions (OH^-) stabilized in the tetragonal form of $BaTiO_3$ at room temperature, and the extraction of the lattice hydroxyl ions (OH^-) helps in the phase transition of $BaTiO_3$.

4. Conclusion

Nanopowders of lead zirconate ($PbZrO_3$) were synthesized by the aqueous co-precipitation method using the KOH mineralizer. The X-ray diffraction showed that the orthorhombic $PbZrO_3$ started to form at 500 °C and formed completely at 900 °C, with a crystalline size of about 9.03 ± 0.2 nm. The intermediate tetragonal (t-ZrO_2) phase was indicated by Raman spectroscopy. Although the powder was calcined at high temperatures, the size of the particles was in nanometer range, when investigated by TEM. The average particle size was found to be 10.44 ± 1.21 nm.

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