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Journal of the European Ceramic Society 26 (2006) 3203–3210

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Influences of water content on synthesis of $(Pb_{0.5},Ba_{0.5})TiO_3$ materials using acetylacetone as chelating agent in a sol–gel process

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Received 16 January 2005; received in revised form 1 August 2005; accepted 9 August 2005
Available online 3 March 2006

Abstract

Ferroelectric $(Pb_{0.5},Ba_{0.5})TiO_3$ (PBT) nanometric sized powders and thin films can be synthesized by a sol–gel process incorporating acetylacetone as a chelating agent to form ligands with titanium isopropoxide. The water contents were varied to investigate the resulting effects on the properties of the PBT powders. It was found that at a lower content of water, a slower rate of hydrolyzation and polycondensation occurred, therefore, a less cross-linking gel that pyrolyzed easily was observed. This less cross-linking gel could be converted to perovskite PBT at temperatures as low as 450 °C. A high purity of perovskite powder was obtained at 500 °C, with a nano-meteric size of about 30–50 nm the specific surface area of 21.91 m^2/g. PBT thin films with polycrystalline or highly preferred orientation were prepared using the as-prepared optimal sol spin coating on (1 0 0) Si or (1 0 0) MgO substrate, respectively. The films were smooth, good quality and crack-free.

Keyword: $(Pb,Ba)TiO_3$; Sol–gel methods; Films

1. Introduction

Lead titanate ($PbTiO_3$) crystallized in a perovskite structure is an important electric material. It can crystallize with alkali earth-metal ion in a solid solution of $(Pb,Ba)TiO_3$,[1] $(Pb,Sr)TiO_3$[2] or $(Pb,Ca)TiO_3$,[3] and its remarkable ferroelectric, pyroelectric and piezoelectric properties are enhanced for applications in opto-electronic, transducers, sensors and non-volatile random access memories (NVRAM). In particular, $(Pb_{1-x}Ba_x)TiO_3$ is an excellent material in microelectric technology to exploit its properties, such as spontaneous polarization, when it is integrated into NVRAM.[4]

The sol–gel process is a good route for powder/thin film preparation due to its low-temperature synthesis, easy-control of composition, and ability to produce fine structures.[5–7] However, the metal alkoxide can react easily with moisture to decrease the solubility of alkoxide in the solvent, so the preparation is inconvenient.[8] However, chelating agents, such as acetic acid,[9,10] 2-methoxyethanol[11–14] and acetylacetone (2,4-pentanedione),[15–17] etc. can ligand with alkoxide to produce a clear precursor, which is insensitive to the moisture in air and make the preparatory procedures easy and cheap.

In particular, acetylacetone is a known chelating agent with metal alkoxides since it significantly changes the hydrolysis behaviors as a nucleophilic reactant and replaces the alkoxy group, thus giving rise to new molecular precursor. In the hydrolysis reaction of ligand acetylacetone, less electronegativity of alkoxy groups are rather quickly removed, while the more electronegative ligand of acetylacetone groups persists as a complex within the metallic group. It has been reported that the use of a modified organometallic precursor leads to better ions homogeneity, enhances the powder's properties, and reduces the powder synthesis temperature.[18]

The most important sol–gel method has been explored by Selvaraj et al.,[19] who obtained oriented $PbTiO_3$ thin-film from solutions of lead acetylacetonate and titanium isopropoxide in 2-methoxyethanol at temperatures as low as 425 °C. The use of lead acetylacetonate as opposed to the more typical lead acetate trihydrate apparently ensured the absence of all traces of water from the solution prior to the hydrolysis step and led to more stable gels. It is not entirely clear why stable gels should result in low temperature crystallization.

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doi:10.1016/j.jeurceramsoc.2005.08.008

One of the many challenges in preparing multicomponent oxides, such as PBT by sol–gel methods is ensuring that all cation species are sufficiently soluble in the solvent of choice, and that they remain stable against rapid hydrolysis, since this leads to flocculation rather than gelation. Hence, the synthesis of PBT by sol–gel methods has been studied to an even lesser extent, with only a few reports. Meng et al.[20] examined particle size effects on Curie temperature for sol–gel prepared materials over the entire range of $Pb_{1-x}Ba_xTiO_3$, although few synthesis details were provided. Giridharan and Jayavel[4] reported the characterizations of $Pb_{0.8}Ba_{0.2}TiO_3$ thin films via a sol–gel route by using acetic acid and 2-methoxyethanol as the chelating agent. More recently, acetylacetone as chelating agent, ethylene glycol as solvent, was identified for producing $Pb_{1-x}Ba_xTiO_3$ precursor sols with good stability, and a highly oriented PBT thin film was successfully manufactured on MgO (1 0 0) substrate.[21] Until now the literature does not, to the best of our knowledge, cover an investigation comparing the influence of water content (the molar ratios of water to titanium isopropoxide) on the hydrolysis and polycondensation of forming perovskite powders from the acetylacetone/ethylene glycol route.

In this study, the $(Pb_{0.5},Ba_{0.5})TiO_3$ ferroelectric powders were fabricated by sol–gel process using ethylene glycol as a solvent. Acetylacetone was used as a chelating agent of $Ti(O\text{-}i\text{-}C_3H_7)_4$, avoiding the high sensitivity of titanium alkoxide reacts with moisture. This investigation focused on the influences of water content for enhancing the characteristics of phase evolution. A nanometric-sized $(Pb_{0.5},Ba_{0.5})TiO_3$ powder was prepared and the optimal sol benefited the preparation of a crack-free thin film.

2. Experimental procedure

2.1. Preparation of nanometric sized $(Pb_{0.5},Ba_{0.5})TiO_3$ powders

Lead barium titanate powders/thin films were prepared with the chemical formula $(Pb_{0.5},Ba_{0.5})TiO_3$. Barium acetate (99%, 2.103 g) was dissolved in ethylene glycol (20 ml). An equal molar quantity of lead acetate (trihydrate 99%, 3.123 g) was dissolved in ethylene glycol (10 ml) on reflux at 120 °C for 1 h to decrease residual water. After reflux, these two acetate solutions were mixed to form a homogeneous Ba–Pb–acetate solution. The two solutions were then mixed to yield a clear 0.125 M solution. Titanium isopropoxide was chelated with acetylacetone (molar ratio of acetylacetone/titanium isopropoxide = 4),[21] to obtain a clear yellow-orange liquid. The resulting titanium compound was then dissolved into the acetylacetone/ethylene glycol solution under vigorous stirring. This solution, containing the cations according to the stoichiometry of $(Pb_{0.5},Ba_{0.5})TiO_3$ being Pb:Ba:Ti = 0.5:0.5:1.00, was refluxed at 120 °C for 4 h to evaporate ethylene glycol and by-products of lower molecular weight. Hydrolysis and gelation were induced by the direct addition of water. The impact of the water content was explored by examining several values of R_w (where R_w = moles ratio of H_2O/titanium isopropoxide). The resultant gels were dried at 130 °C for 2 days, and then calcined at various temperatures for 5 h to examine crystallization behavior. The flow chart of nanometric sized $(Pb_{0.5},Ba_{0.5})TiO_3$ powder preparation is shown in Fig. 1.

The optimal preparatory conditions of powders was obtained from the above experiments and used to prepare a sol for the manufacturing of thin films. A suitable viscosity of sol applied for spin-coating on Si (1 0 0) or MgO (1 0 0) substrate was obtained by gelation at 120 °C for 4 h for further hydrolysis and polycondensation. This sol can be kept at room temperature for at least 12 months, maintaining a moderate viscosity, so that it still can be applied for spin-coating to produce a thin film.

2.2. Synthesis of $(Pb_{0.5},Ba_{0.5})TiO_3$ thin film on Si (1 0 0) or MgO (1 0 0) substrate

Prior to coating, the Si (1 0 0) or MgO (1 0 0) substrates (10 mm × 10 mm) were thoroughly cleaned. Inorganic contaminations were removed in a solution containing H_2O:NH_4OH:H_2O_2 and H_2O:HCl:H_2O_2 in the volume ratio of 10:1:1, respectively. Organic contaminations were removed in boiling acetone and ethanol. Finally, the substrates were then washed in deionized water and dried.

The as-prepared sols were spin-coated on the substrates using a spin coater at 4000 rpm and 30 s for each coating. The as-deposited films were then dried at 450 °C on a hot plate for 3 min to evaporate residual organic species. The films were heat-treated at 600 °C for 2 h at a heating rate of 10 °C/min, and a cooling rate of 5 °C/min was used to prevent the cracking of thin films.

However, the dried gels/as-deposited films were heat-treated at various temperatures in an electric furnace. Due to the fact that considerable amounts of PbO evaporate at high temperature, a method similar to the one applied by Snow,[22] which compensates for the PbO loss, had to be applied. The dried gels/as-deposited films were heat-treated on an Al_2O_3 plate covered by an aluminum oxide crucible, under an atmosphere containing PbO. The partial pressure of PbO was generated by a solid mixture of 90% PBT and 10 wt.% PbO.

2.3. Testing methods

The Pb-Ba-Ti-gels were dried at 130 °C for 8 h to evaporate the residual solvents. Then, the dried gel was probed by Fourier transfer infrared (FTIR) spectroscopy using a Nicolet spectrometer over the wave number range 4000–400 cm^{-1}. Thermal decomposition characteristics of the gel were studied by simultaneous differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA, Netzsch STA-449) at a constant heating rate of 10 °C/min under an argon atmosphere. Powders were examined by X-ray diffraction (XRD) (Bruker D8 Discover), laser particle size distribution analysis (GALAI-CIS-1), field-emission scanning electron microscopy (FE-SEM/EDX, Leo Analytical), and Brunauer, Emmett and Teller (BET) specific surface area analysis (BET) (Gemini 2360). Furthermore, the crystalline phase of the PBT films formed on Si (1 0 0) or MgO (1 0 0) substrates were examined

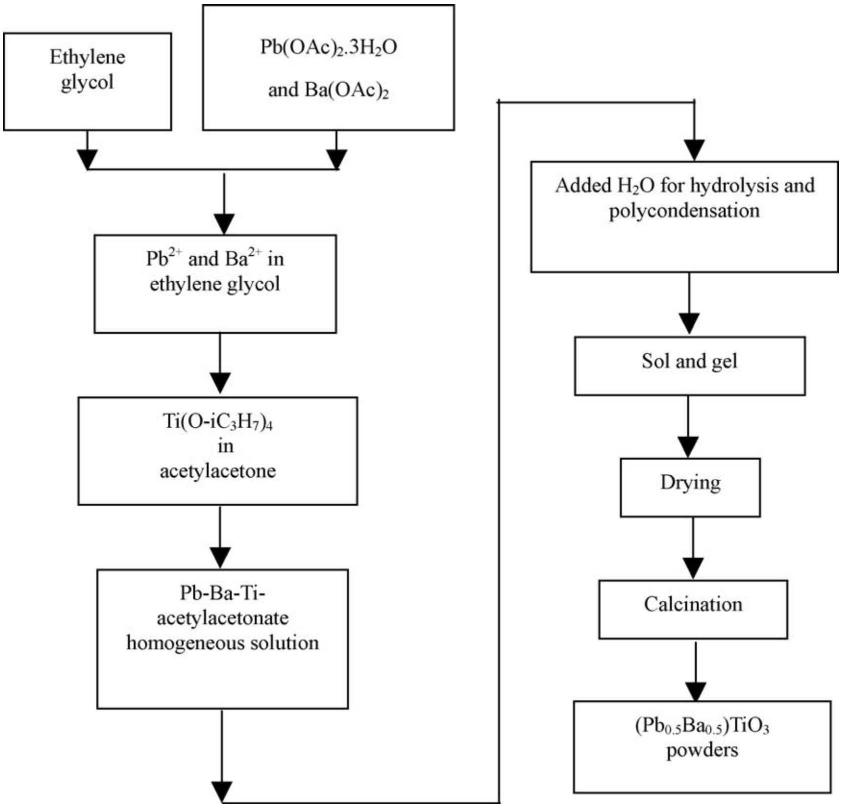

Fig. 1. Schematic illustration of the preparations of $(Pb_{0.5},Ba_{0.5})TiO_3$ powders by a sol–gel process.

using XRD, and the microstructures of the films were observed using SEM.

3. Results and discussion

3.1. Chemical and physical properties of Pb-Ba-Ti-gels

Fig. 2 shows the TGA characteristics of the Pb-Ba-Ti-gels gelated at 120 °C and then dried at 130 °C. Two major weight loss events are apparent in the TGA data. The first, occurring over the temperature range 100–250 °C, is due to the evaporation of water and solvents. In the second stage, a distinct weight loss occurred in the TGA analyses between 250 and 450 °C for the combustion of organic groups in the cross-linked gels.[23] The sample prepared using more water content ($R_w = 50$) has the least weight loss, at 14%. The sample obtained without any water added ($R_w = 0$) exhibited the highest weight loss, about 27%. In addition, the weight loss of $R_w = 17$ at 24% and $R_w = 30$ at 17%, were between those for $R_w = 50$ (14%) and $R_w = 0$ (27%), respectively.

It is found that there is an increase of weight loss with the decrease of R_w, revealing that the gel synthesized from relatively lower water content contained much more organic substances (particularly the ligand acetylacetone), results in an inhibition of the hydrolysis and condensation reaction. Acetylacetone inhibits the process of condensation, extends the gel time, and leads to form smaller gels. However, increasing R_w would be expected to increase the level of hydrolysis and increase the amount of ROH or RCOOH produced. These volatile species could then have been eliminated by evaporation prior to running TGA. The weight fraction of ROH and RCOOH measured by weight loss of gels dried at 130 °C was about 10%, 13% and 17%, for $R_w = 17$, 30 and 50, respectively. In contrast, the amount of acetylacetone is small in the Pb-Ba-Ti-gel obtained from higher water content, owing to the hydrolysis reaction proceeds to greater extents, resulting in larger particle size of the gel. In addition, weight loss was much more moderate at 600 °C under all conditions,

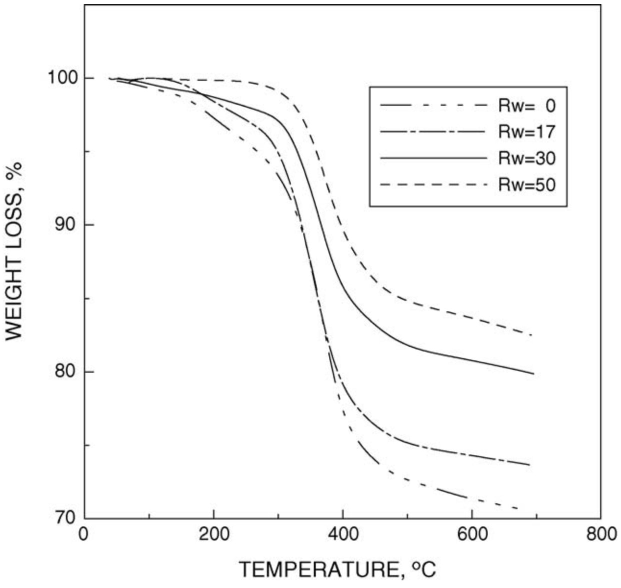

Fig. 2. TGA analyses of dried gel prepared at various water contents.

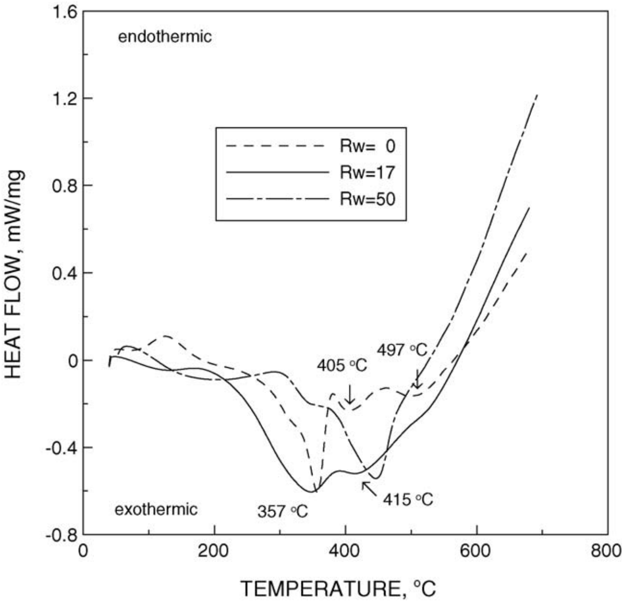

Fig. 3. DSC analyses of dried gel prepared at various water contents.

and the remaining powders were only a trace of carbonate, as determined by FTIR.

Fig. 3 shows the DSC results of gels obtained from various water contents. The endothermic peak in the vicinity of 130 °C is the vaporization of water and constituents of alcohol. The first exothermal peak at about 360 °C is the combustion of organic species, and the exothermal peaks around 400–500 °C were attributed to the formation of an intermediary phase and perovskite phases.

Comparing the results of DSC data of the first exothermal peak at around 360 °C, the lower water content ($R_w = 17$) there is much more heat flow, revealing that more organic substances (about 80 ± 5 wt.% ligand acetylacetone) are contained in the gel structure. A much higher ratio of acetylacetone in the structure of the dried gel indicates that the rate of polycondensation is probably lower. On the other hand, at a higher water content of $R_w = 50$, there is less heat flow observed from DSC data, indicating that there was a small portion of acetylacetone ligand in the gel. Acetylacetone in the structure is easily expelled since the rate of condensation is more rapid. It is worth noting that an additional exothermal peak at 405 °C exhibited in the sample without any water added ($R_w = 0$) was identified to be the formation of carbonate by the studies of FTIR, DSC and XRD as shown below.

There is also an obviously difference of the peak at 415–500 °C, which is assigned the formation of perovskite phase. It indicates that the exothermic peaks of the gels prepared at $R_w = 0$, 17 and 50, are 497 °C, 415 °C and 450 °C, those peaks seem broad for the crystallization of perovskite. Furthermore, it is also indicated that the perovskite phase could be produced more easily as a lower water content applied. At a lower water content ($R_w = 17$), the perovskite phase powder can be obtained at temperature as low as 450 °C, which will be coincided with the studies of XRD as shown below.

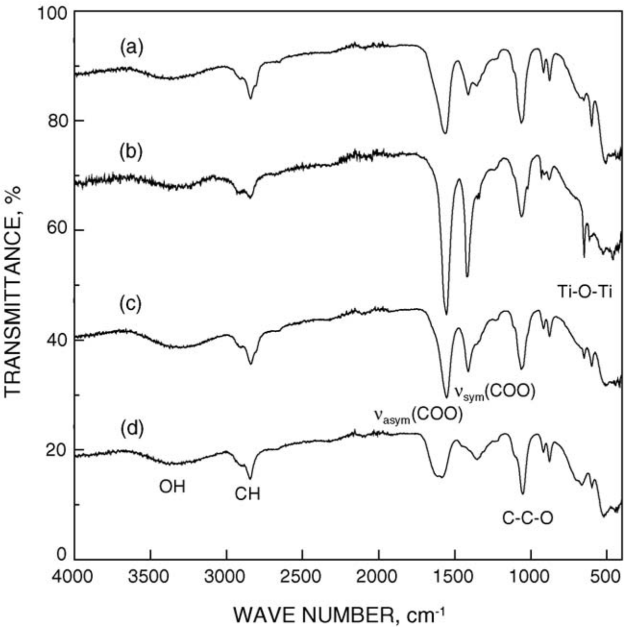

Fig. 4. The FTIR spectra of gel dried at 130 °C: (a) $R_w = 0$ gelated at 120 °C; (b) $R_w = 17$ gelated at 120 °C; (c) $R_w = 50$ gelated at 120 °C; and (d) $R_w = 0$ gelated at 150 °C.

The FTIR spectra of the dried gel obtained from various water contents are shown in Fig. 4. The FTIR data indicates that there are two absorption bands at around 1560 and 1410 cm^{-1} for the gels gelated at 120 °C (Fig. 4(a)–(c)). The two peaks have also been observed in the sol–gel processing of acetate-containing systems and have been attributed to asymmetric and symmetric stretching modes of –COO$^-$.[24,25] These bands, as well as those associated with the acetylacetone ligand, disappear after heat treatment at temperatures above 450 °C, clearly revealing the formation of a residual carbonate phase in calcined gels of 1445 cm^{-1} (not shown). Additionally, the absorption peak of C–C–O of ethylene glycol is about 1080 cm^{-1}.[26] It has been reported that when the bidentate ligand difference ($\Delta\nu$) of these two absorption bands of asymmetric and symmetric vibrations is >160 cm^{-1}, it is a typical bridging bidentate ligand. When $\Delta\nu$ is small than 80 cm^{-1}, it is a chelating bidentate ligand.[24]

As seen from Fig. 4(d), the broader absorption bands at 1610, 1560 and 1330 cm^{-1} exhibit some shoulders and show two $\Delta\nu$ at 280 and 230 cm^{-1}, respectively, suggest that the gels contained two types of bridging ligands.[25] It is much larger than those $\Delta\nu$ values obtained from gels gelated at 120 °C (Fig. 4(a)–(c)). The broader absorption bands with larger $\Delta\nu$ reveals that the gel gelated at 150 °C was much cross-linking. In addition, the decrease in intensity of absorption bands at 1610, 1560 and 1330 cm^{-1}, revealing those corresponding to the ligand acetylacetone decrease when the gelation temperature up to 150 °C.

It has been reported that a larger $\Delta\nu$ indicates a more highly bridging bidentate ligand, which leads to a larger portion of cross-linking and more difficult pyrolyzation of the Ti–O–C bonding. As a result, a higher formation temperature of perovskite phase as well as a bigger particle size of powder can be expected.[27] This will be demonstrated by the SEM and XRD investigations of powder as shown below. However, the phenomena were in good agreement with observing the fact of a shorter gelation time in this case. Nevertheless, the gel gelated also examined by SEM showed a bigger particle size in the dried gel (not shown).

In Fig. 4(a), the absorption bands at around 571, 463 and $438\,\mathrm{cm}^{-1}$[26] are more ambiguous than those observed from Fig. 4(b)–(d), revealing that a relatively lower fraction of Ti–O–Ti existed in the gel produced without water added ($R_w = 0$). A higher fraction of Ti–O–Ti structure in the cross-linking gel makes a more homogeneous mixing of cations (Pb^{2+}, Ba^{2+} and Ti^{4+}), due to the ligand of acetylacetone. Thus, this would be understood to mean that the perovskite phase obtained from the amorphous gel is much significant segregation of the individual metal ions than those gels obtained from water added.

Fig. 5 shows the XRD data as a function of calcination temperatures for the dried gel prepared at $R_w = 17$. The powders were amorphous if calcined at temperatures below 400 °C. This indicates that the precursor gels had started to crystallize via an intermediary phase at 450 °C, and at this temperature there is still some unreacted carbonate. These results are consistent with the DSC analyses, as shown above. At 600 °C the gel contained a higher amount of perovskite phase and fewer unreacted $BaCO_3$, $PbCO_3$ and TiO_2.

The studies of DSC and XRD revealed that PBT polycrystal perovskite phase accompanied with a few unreacted species was obtained from the gels calcined at 500–600 °C. As the calcined temperature increased, carbonates that reacted with TiO_2 became a highly pure PBT perovskite structure. Furthermore, the peak due to the perovskite phase became stronger and sharper as the calcination temperature increased from 500 to 600 °C, indicating an increase in the degree of long-range order in the perovskite lattice.

As seen from the XRD patterns in Fig. 5, there is only a small amount of $BaCO_3$, and only a trace of TiO_2 and $Pb_2Ti_2O_6$ observed as intermediate phases prior to the formation of pure PBT perovskite phase during the decomposition of the dried gel. Only traces of $BaCO_3$, $Pb_2Ti_2O_6$ and TiO_2 remaining should be considered as an almost perfect mixing of the constituent cations in the gels. This can indicate that the perovskite phase is obtained from the amorphous powder precursor without significant segregation of the individual metals directly.

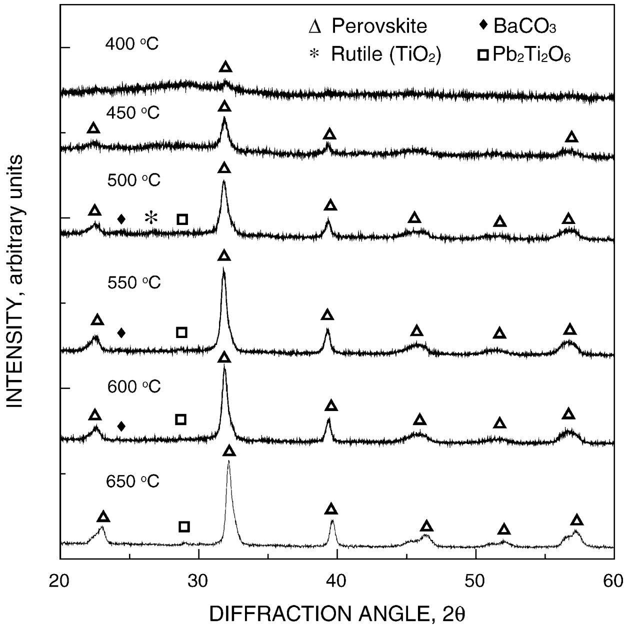

Fig. 5. The XRD patterns of the dried gel obtained from $R_w = 17$ and calcined at various temperatures.

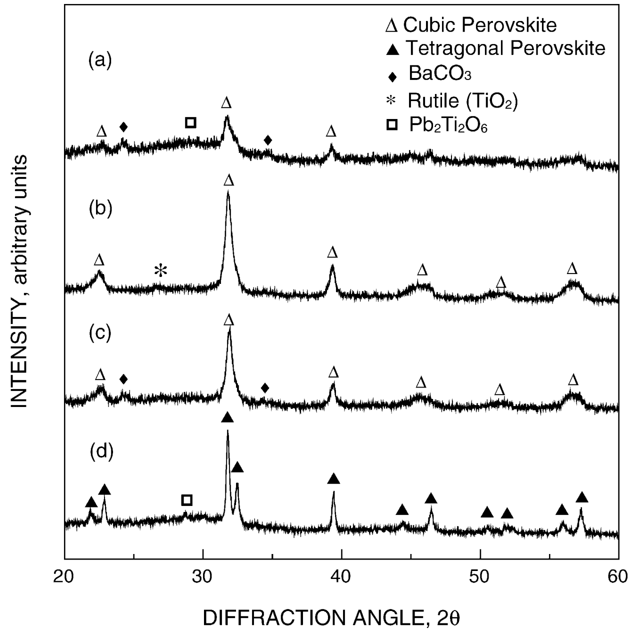

Fig. 6. The XRD patterns of calcined $(Pb_{0.5},Ba_{0.5})TiO_3$ powders: (a) the powder prepared at $R_w = 0$, gelated at 120 °C and calcined at 500 °C; (b) the powder prepared at $R_w = 17$, gelated at 120 °C and calcined at 500 °C; (c) the powder prepared at $R_w = 50$, gelated at 120 °C and calcined at 500 °C; (d) the powder prepared at $R_w = 0$, gelated at 150 °C and calcined at 650 °C.

The samples prepared from different water contents calcined at 500 °C are also shown in Fig. 6. The XRD analyses shows that the sample obtained without water added exhibits less intensity of perovskite and is accompanied by $BaCO_3$ and $Pb_2Ti_2O_6$. The powder obtained from a lower water content ($R_w = 17$) and calcined at 500 °C, a relatively higher purity of perovskite is observed. In contrast, the powder obtained from a higher water content ($R_w = 50$), a perovskite phase containing $BaCO_3$ and $Pb_2Ti_2O_6$ are also examined. Here, the second phases could have been caused by the more difficult pyrolyzing of a more highly cross-linked gel, which was obtained from the high water content. Furthermore, the XRD results are supported by FTIR measurements. The FTIR spectrum of $(Pb_{0.5},Ba_{0.5})TiO_3$ is characterized by a broad absorption band in the range of $500–530\,\mathrm{cm}^{-1}$, which is attributed to a TiO_6 octahedral stretching model.[28] Carbonate absorbs broadly at $1445\,\mathrm{cm}^{-1}$ and sharply at 1064, 860 and $693\,\mathrm{cm}^{-1}$ (not shown). These results also coincide with the studies of DSC/TGA.

In particular, the XRD patterns of the gel prepared without water ($R_w = 0$) and gelated at 130–150 °C is different from the others, since it was amorphous at calcination temperatures below 650 °C (not shown). As calcined at 650 °C it converted to a tetragonal perovskite structure (Fig. 6(d)). Comparing with the

Table 1
The powder properties of nanometric-sized $(Pb_{0.5},Ba_{0.5})TiO_3$ powders prepared from various water contents and calcined at 500 °C

	D_{SEM} (nm)	S_{BET} (m^2/g)	D_{LPD} (nm)	D_{LPD}/D_{SEM}
$R_w = 0$	45–85 (65 ± 20)	18.66	355	5.46
$R_w = 17$	30–50 (40 ± 10)	21.91	144	3.60
$R_w = 30$	40–70 (55 ± 15)	19.67	243	4.42
$R_w = 50$	40–80 (60 ± 20)	16.24	361	6.02

studies of FTIR, the $\Delta\nu$ of Fig. 4(d) is typically larger than the others. This reveals that there is much cross-linking structure in the gel, leading to a need for higher temperature to break the Ti–O–C bonding. Therefore, the formation temperature of perovskite phase is higher than those of other cases. Furthermore, the gel gelated at 150 °C and then calcined at 650 °C, the particle size of PBT powder was about 0.2–0.4 µm, which was much bigger than those powders of nanometric-sized scale. Thus, the tetragonal perovskite structure can be explained by the crystallite size effect.

3.2. *Characterizations of $(Pb_{0.5},Ba_{0.5})TiO_3$ powders*

The $(Pb_{0.5},Ba_{0.5})TiO_3$ powders prepared from $R_w = 17$ calcined at 500 °C were examined by SEM, BET specific surface area analyzer and laser particle size distribution analyzer, respectively; and are listed in Table 1. The specific surface area of the PBT powder is 21.92 m^2/g and the particle size of the nanometric sized powder is 30–50 nm. Table 1 shows that the mean particle size obtained by SEM (D_{SEM}) is smaller than that obtained by the laser particle size distribution analyzer (D_{LPD}) for the calcined perovskite powders. This means that the higher water contents lead to the formation of larger crystals and the agglomeration process is also promoted. This can be seen by calculating the ratio D_{LPD}/D_{SEM}.

Fig. 7 shows the SEM images of the $(Pb_{0.5},Ba_{0.5})TiO_3$ powders prepared at various molar ratios of water content, at $R = 0$, 17, 30 and 50, respectively, and calcined at 550 °C. The primary particle sizes are small but aggregated, having primary particle sizes of 55–95, 30–60, 40–80 and 50–90 nm, respectively. This result confirms that the powders prepared by the acetylacetone/ethylene glycol sol–gel method in the present work are perovskite phase materials of nanometer size. This study shows that the particle sizes of the formed powders are dependent on the amount of water content in the sol–gel process. The obtained particle size of $(Pb_{0.5},Ba_{0.5})TiO_3$ powder is increased as the amount of water content increased. These results suggest the relationship with the morphology of the precursor gel and calcined powder. The particle size of the gel is smaller for lower water content and the particle size of the powder calcined from gel is also very fine. The FTIR spectra of the dried gel prepared at various water contents (shown in Fig. 4) shows that the gel of lower water content demonstrating smaller $\Delta\nu$ has a lower rate of cross-linking and a smaller particle size of precursor gel. This lower water content makes it is easier to have a more chelating coordination. Hence, the particle size of PBT powder obtained from the calcination of a less cross-linking gel also contains smaller particle size. On the other hand, the

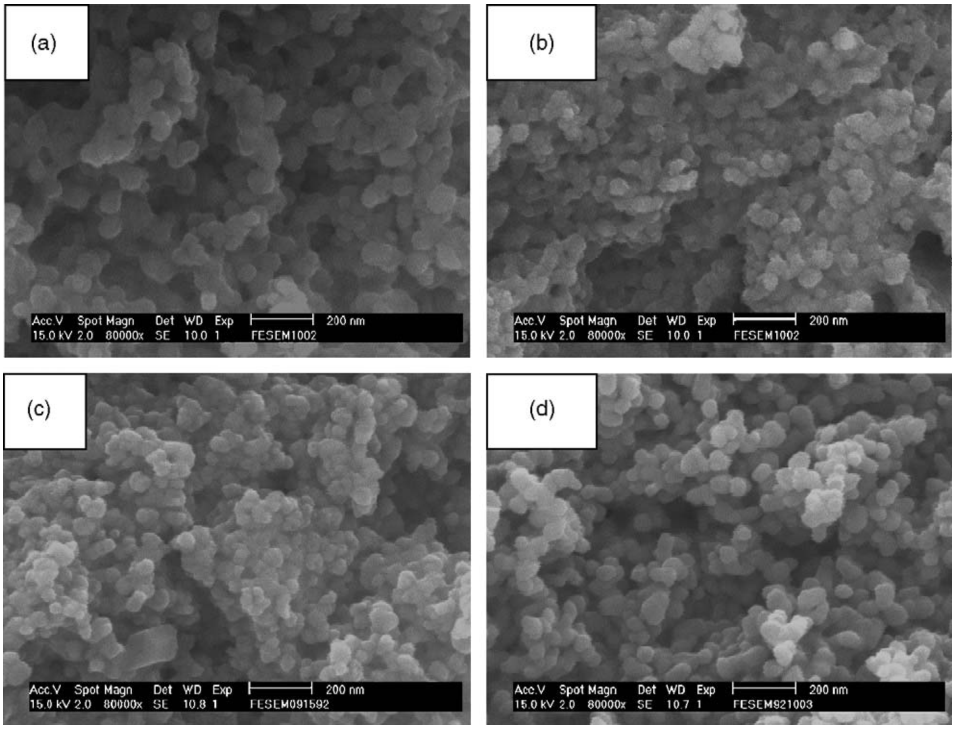

Fig. 7. SEM micrographs of $(Pb_{0.5},Ba_{0.5})TiO_3$ powders prepared from various water contents and calcined at 550 °C: (a) the molar ratio of water to titanium isopropoxide at 0; (b) the molar ratio of water to titanium isopropoxide at 17; (c) the molar ratio of water to titanium isopropoxide at 30; and (d) the molar ratio of water to titanium isopropoxide at 50.

higher water content makes a more bridging bidentate coordination. When there are more bridging structures, a higher rate of cross-linking of the gel, and a bigger particle size of gel makes the gel calcined to a bigger particle size of $(Pb_{0.5},Ba_{0.5})TiO_3$ powder.

3.3. Preparation of $(Pb_{0.5},Ba_{0.5})TiO_3$ thin films

By using modified solvent of ethylene glycol dissolved lead and barium acetate in a minimum amount, the $(Pb_{0.5},Ba_{0.5})TiO_3$ could be prepared without any detectable precipitation after stock precursor solution was kept at room temperature for 12 months. For the thin film preparation, when the heating temperature is high, the heterogeneous nucleation and growth of perovskite grain at the interface between the film and the substrate occur easily because of high thermal energy. The processing temperature used in this study was 150 °C higher than crystallization temperature (about 450 °C) obtained from the powder studies as described above. Thus, the heat treatment temperature of PBT thin film was 600 °C.

Two sols, a clear one obtained from a suitable gelation time of 4 h and another one containing a little precipitation from a longer gelation time of 6 h, were used for spin coating on Si (1 0 0) and MgO (1 0 0) substrates, respectively. The films as examined by XRD are shown in Fig. 8. The examination of XRD indicates that polycrystal thin films were prepared on Si (1 0 0) substrate in spite of a clear sol or sol containing a few precipitate applied, as shown in Fig. 8(a) and (b), respectively. Similarly, a polycrystal PBT thin film was synthesized on MgO (1 0 0) from the sol containing a few precipitate, as shown in Fig. 8(c). It is worth noting that a preferred oriented PBT film can only be obtained from clear sol spin coated on MgO (1 0 0) substrate, as shown in Fig. 8(d). This may be because when Pb-Ba-Ti-sol is spin coated on Si (1 0 0), is difficult to get a thin film with highly preferred orientation, due to the lattice constant mismatch of $(Pb_{0.5},Ba_{0.5})TiO_3$ and Si (1 0 0). Nevertheless, the sol containing a small amount of precipitate also indicated that a preferred oriented thin film can not be obtained even on a MgO (1 0 0) substrate. This explains that the precipitate of sol supplies a nucleation site and leads the crystallization along the nucleation site on the precipitate, rather than the MgO surface, resulting in the formation of a polycrystal $(Pb_{0.5},Ba_{0.5})TiO_3$ thin film. In contrast, in the clear sol on MgO (1 0 0), a nucleation site on MgO (1 0 0) during annealing causes the crystallization to be built along the matched lattice, resulting in highly oriented PBT thin films.

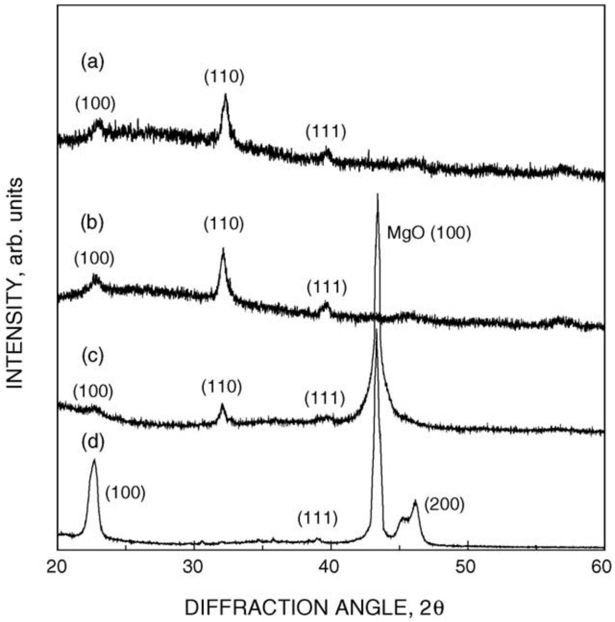

Fig. 8. XRD patterns of $(Pb_{0.5},Ba_{0.5})TiO_3$ films prepared from various sols and substrates then annealed at 600 °C: (a) sol containing a few precipitate spin coating on Si (1 0 0); (b) clear sol spin coating on Si (1 0 0); (c) sol containing a few precipitate spin coating on MgO (1 0 0); and (d) clear sol spin coating on MgO (1 0 0).

SEM images of the surface of a three-layer coating film prepared from MgO (1 0 0) substrate and annealed at 600 °C for 2 h at a heating of 10 °C/min are shown in Fig. 9. In Fig. 9(a), it reveals that the surface of the film is crack-free, showing that the sol prepared from acetylacetone/ethylene glycol can be utilized to produce smooth, good quality and crack-free $(Pb_{0.5},Ba_{0.5})TiO_3$ thin films. Besides, the surface of the as-deposited film is smooth with smaller porosity and grain size of 40–80 nm as shown in Fig. 9(b).

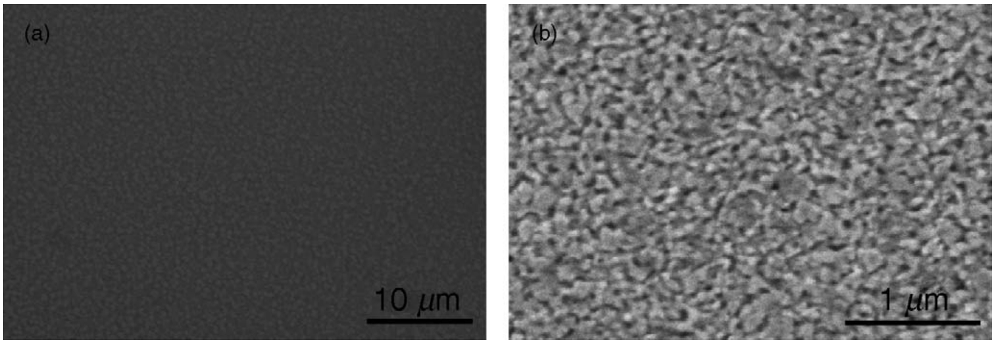

Fig. 9. SEM images of $(Pb_{0.5},Ba_{0.5})TiO_3$ films prepared from clear Pb-Ba-Ti-sol coating for three layers and annealed at 600 °C on MgO (1 0 0) substrate: (a) at a lower magnificence of 2000 and (b) at a higher magnificence of 30,000.

4. Conclusions

$(Pb_{0.5},Ba_{0.5})TiO_3$ nanometric-sized powders and thin films can be obtained from acetylacetone/ethylene glycol by a sol–gel process, in which acetylacetone was used to chelate with titanium isopropoxide avoiding the sensitivity of the moisture in air. FTIR, DSC/TGA, SEM and XRD, etc. were utilized to investigate the effects of water content on the formation and properties of the perovskite powders. It was found that with lower water content, hydrolysis and polycondensation occurred more slowly. Therefore, a less cross-linking gel that was easily pyrolyzed was observed. Nevertheless, less cross-linking gel can be converted to perovskite phase at temperatures as low as 450 °C. The high purity of the perovskite powder obtained at 500 °C, exhibited a nanometric size of about 30–50 nm and the specific surface area was 21.91 m^2/g. Polycrystal and thin films with highly preferred orientation were prepared by using the as-prepared optimal sol spin coating on (1 0 0) Si and (1 0 0) MgO substrates, respectively. Both of the films annealed at 600 °C had good quality of crystallinity, and were smooth and crack-free, indicating that the use of acetylacetone/ethylene glycol is an excellent technique of sol–gel method for the preparation of PBT thin films.

Acknowledgments

One of the authors thanks the National Kaohsiung University of Applied Science, in Taiwan ROC, for financial support of his work as a visiting scholar at Caltech, USA. In addition, this work has been funded by the United States Department of Defense MURI award administered by the Army Research Office. Additional support has been provided by the National Science Foundation, through Caltech Center for the Science and Engineering of Materials.

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