

Effect of drying temperature on structure, phase transformation of sol–gel-derived lead zirconate titanate powders

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Abstract

Lead zirconate titanate (PZT) (53/47) powders were prepared by a cheating acetate sol–gel process. The drying temperature effect on crystallization behavior was conducted to determine the best conditions for preparing high content of perovskite PZT powders in the morphotropic region. DSC/TG analysis, FT-IR spectrum and X-ray diffraction were carried out to identify the reaction sequences and calculated the activation energy of every transition temperature during the drying procedures. In the present work, well-crystallized, single-phase perovskite PZT powders were obtained after drying PZT stock solution at 300 °C for 1 h, then heat treatment at 600 °C for 30 min. The dependence of this crystallization temperature on the drying conditions was discussed.

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1. Introduction

Lead zirconate titanates (PZT, $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$) are of great interest due to their excellent piezoelectric properties [1]. PZT-based materials are widely used in transducers, ferroelectric memories, optical filters, shutters, actuators and modulators. PZT exhibits non-centrosymmetric perovskite structure below its Curie temperature ($T_C = 350$ °C). The electromechanical response of these ceramics is maximum when x lies near the composition of the morphotropic

phase boundary (MPB) which separates the tetragonal (T) and rhombohedral (R) phases from Ti- to Zr-rich regions, respectively. At the MPB composition, PZT exhibits the best piezoelectric properties.

High quality PZT powder is the important criterion to fabricate the superior piezoelectric PZT ceramic materials. PZT powders are usually prepared by solid-state reaction from their constituent oxides [2,3]. However, the presence of intermediate reactions between these oxides results in compositional secondary phases and fluctuations [2,4,5]. In contrast to the conventional solid-state reaction methods, wet chemical route allows mixing of the component in the molecular level, resulting in materials with high compositional homogeneity and low sintering temperatures. The alkoxide-based sol–gel process is one of the most promising methods for synthesizing ceramic powders.

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Titanium and zirconium are the electropositive features, which present highly polar M–O (M means titanium or zirconium) bonds. It means that titanium and zirconium alkoxides are extremely reactive towards water. In order to control the undesired hydration from the moisture, it is important to add some chelating agent into the PZT solution. Several researches [6–9] reported that acetic acid can inhibit the uncontrolled hydration of alkoxides on the preparation of PZT powders by sol–gel. Among various acids, acetic acid is commonly used. The role of the acetic acid represent as a chemical modifier [6], chelating agent [7] or stabilizers [8,9]. Before the hydration and condensation process by adding water into the sol–gel-derived solution, the addition of the acetic acid acts as a chemical modifier by promoting a ligand exchange between the alcohol groups of the alkoxides and the acetate groups of the acetic acid, resulting in a relative moisture insensitive precursor. The addition of acetic acid indeed is a key factor to prepare the highly stable PZT solution against moisture from the atmosphere [6–9].

Several researchers [10–13] had reported that by the DTA/TGA analysis of PZT gels, there is an endothermic peak at 150 °C which is attributed to the evaporation of solvents with low boiling point temperature and an exothermic peak exists at 300–360 °C, which is attributed to the decomposition of organic compounds [14]. Pyrolysis of dried PZT gels is an important step on the way from metallo-organic, amorphous precursors to inorganic ceramic materials. PZT powders derived by sol–gel method are dried in two or more stages in order to remove solvent completely [12]. But, fewer studies focused on the effect of drying conditions of the PZT powders. In order to identify the various drying conditions thoroughly, we designed a new drying process depending on the pyrolysis temperature of PZT gels in order to obtain a homogeneous oxide mixture.

The present study concerns the preparation of PZT powders via the acetate sol–gel method. Acetic acid was used as a chelating agent. Two drying temperatures (150 and 300 °C) are applied in the study. The effect of drying temperature on the crystallization behavior, the activation energies of pyrolysis reactions and phase transformation are discussed in the study.

2. Experimental procedures

2.1. Powder preparation

Lead acetate trihydrate [Pb(CH₃COO)₂·3H₂O, SHOWA, 99.5%], zirconium *n*-propoxide [Zr(OC₃H₇)₄, STREM chemicals, 75%] and titanium iso-propoxide [Ti(OCH(CH₃)₂)₄, ACROS organics, 98%] were used as sources of lead, zirconium and titanium to prepare PZT precursor solution. The whole process of the preparation of the precursor solution is conducted in an ambient atmosphere.

Firstly, lead acetate trihydrate was dissolved in *n*-propyl alcohol (C₃H₇OH, ACROS organics, 99%) with the ratio of 10 g:1 ml at 80 °C in a three-neck reaction glass beaker. Then,

the solution was heated to approximately 120 °C and maintained for 2 h to remove the residual water and cooled in air to 80 °C. A stoichiometric amount of zirconium *n*-propoxide and acetic acid (CH₃COOH, TDIA, 99.9%) was added to the lead acetate solution and refluxed at 120 °C for 1 h to form PZ solution. The ratio of lead acetate to acetic acid to *n*-propyl alcohol is 10:5:1. After that, titanium iso-propoxide was added to the PZ solution and further refluxed at 120 °C for 2 h to form the PZT (Zr/Ti = 53/47) solution.

PZT stock solution was used to produce dried gels which were dried at 300 °C for 1 h, defined as the H.T. dried gels and at 150 °C for 10 h, defined as the L.T. dried gels, respectively. Finally, the dried gels were ground and calcined from 400 to 600 °C for 30 min.

2.2. Characterization

The thermal properties of the gel powders were analyzed using differential scanning calorimeter/thermo-gravimetric analysis (DSC/TGA, Setaram Labsys-TGDSC DSC131, France), with various heating rates from 2.5 to 20 °C/min. The bonding conditions of the calcined PZT powders were obtained by using a Fourier transform infrared spectrometer (FT-IR, JASCO FT-IR-460 plus, Japan) with a frequency ranging from 400 to 4000 cm⁻¹. The crystal structures of calcined PZT powders were identified by X-ray diffractometer (XRD, Rigaku Geiger Flex, Japan) with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) and a scanning step of 4°/min and 2 θ angle from 20° to 60°.

3. Results and discussion

Fig. 1 shows the results of DSC and TGA analysis of the H.T. and L.T. dried gels. The terms 1–3 and A–E indicate the endothermic and exothermic peaks in Fig. 1. The curve in Fig. 1 can be divided into three regions. Region I, which is from room temperature to 200 °C, refers to the evaporation of solvents as water or alcohol and region II ranges from 200 to 400 °C which is responsible for the decomposition of organics as lead acetate. Region III, as the temperature above 400 °C, defined as phase crystallization region of the pyrochlore and perovskite phase. The DSC curves show two endothermic peaks (i.e. peak 1 and peak 2) for both the H.T. and L.T. dried gels below 100 °C, which are corresponding to the removal of solvent and/or moisture physically adsorbed on the surface of the gels. Endothermic peak 3 appears at 204 °C, which is ascribed to melting of the anhydrous lead acetate [Pb(CH₃COO)₂] [15]. The TGA curves (Fig. 1(b)) shows no weight loss at the endothermic temperature. Furthermore, the DSC curves for various heating rates as shown in Fig. 2 indicate the reaction occurred at 204 °C keep in the same temperature when the heating rate increases. It implies that the reaction at that temperature is a pure physical reaction. Peak A is responsible for the decomposition reaction of the anhydrous lead acetate to the two kinds of

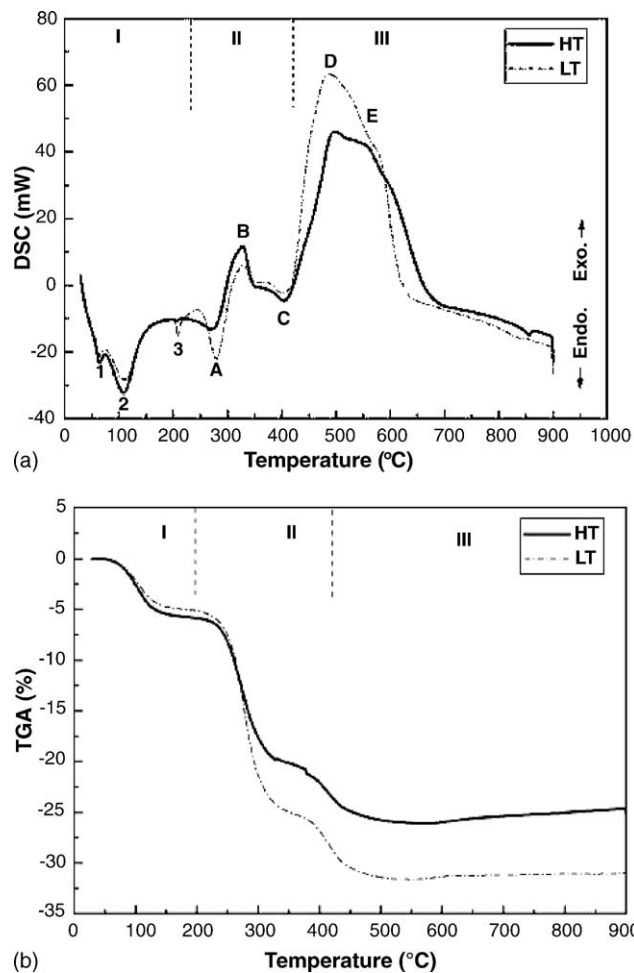


Fig. 1. (a) DSC and (b) TGA curves of H.T. and L.T. dried gels.

intermediate basic acetate salts, $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot \text{PbO}$ and $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 2\text{PbO}$ [15,16]. The endothermic reaction is in good agreement with the previous studies [15,16]. According to the reports [16,17], the major part of organic components in the PZT dried gels are the acetate groups incorporated from the lead acetate and the dynamic fragmentation pattern for acid-catalyzed PZT gels was quite similar to that for pure lead acetate trihydrate [17]. According to the high similarity of the IR spectra [16] of lead acetate and PZT dried gels in the carbonyl stretching region, the acetate groups are bounded to Pb^{2+} mostly in the dried gels. Nevertheless, small amount of acetate groups could also be connected to zirconium or titanium [16]. The DSC curve shows the L.T. dried gel has a stronger endothermic reaction than H.T. gel for peak A. Because the H.T. dried gels had been preheated at 300°C for 1 h, partial acetate groups were removed by the heat treatment. The dominant endothermic reaction for the H.T. dried gels is the decomposition of $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot \text{PbO}$ to $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 2\text{PbO}$. On the other hand, the L.T. dried gels consist of $\text{Pb}(\text{CH}_3\text{COO})_2$ to $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot \text{PbO}$ and $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot \text{PbO}$ to $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 2\text{PbO}$. The lack of heat treatment at 300°C for the L.T. dried gels lead to

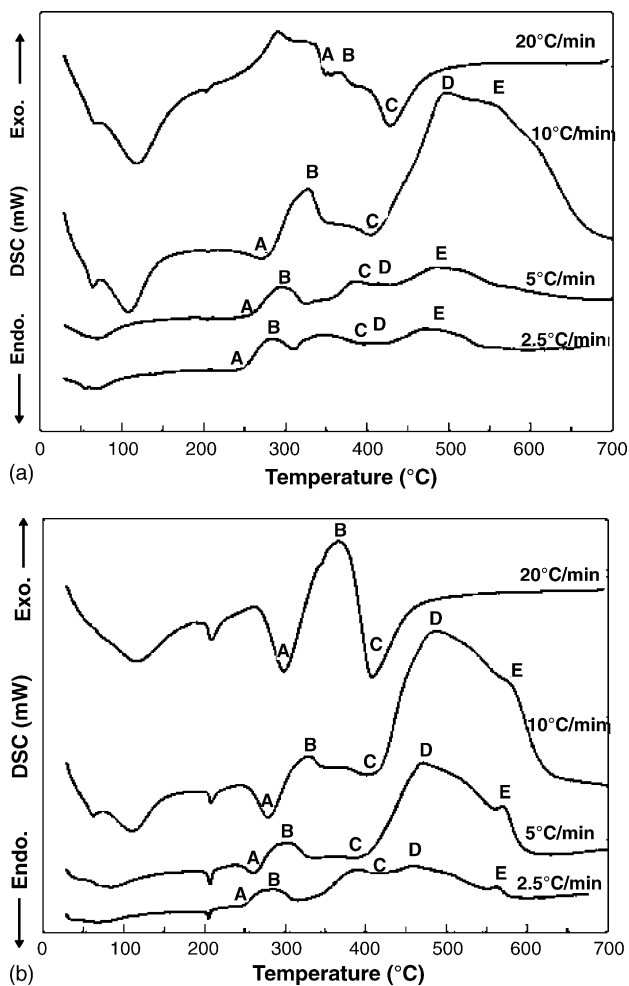


Fig. 2. DSC curves of: (a) H.T. gels and (b) L.T. dried gels at different heating rates.

the more complex decomposition reactions and a stronger endothermic reaction peak (Fig. 1(a)).

According to Merkle and Bertagnoli [16], the strong exothermic peak B in Fig. 1 for both the H.T. and L.T. dried gels is due to the decomposition of $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 2\text{PbO}$ to $\text{PbO}_{1-x}(\text{CO}_3)_x$. It can be seen that the exothermic peak of H.T. ones have a higher intensity. Because the weak-binding acetic acid and/or acetate groups in the H.T. dried gels had been removed by preheating at 300°C for 1 h, the reaction occurs at peak B for the H.T. series is only the formation of $\text{PbO}_{1-x}(\text{CO}_3)_x$. Otherwise, for the L.T. ones, the incomplete removal of the acetic acid and/or acetate groups will lead to partial endothermic decomposition reaction for lead subacetate, similar with the reactions of the peak A mentioned above. These reactions will reduce the intensity of the exothermic peak B. Peak C is considered as the formation of PbO phase and it will be confirmed by the XRD analysis as shown in Fig. 4 [15]. For the L.T. dried gels, the peak C has a smaller intensity than that of the H.T. ones. Peaks D and E are assigned as the formation of the pyrochlore and perovskite phase [17–23].

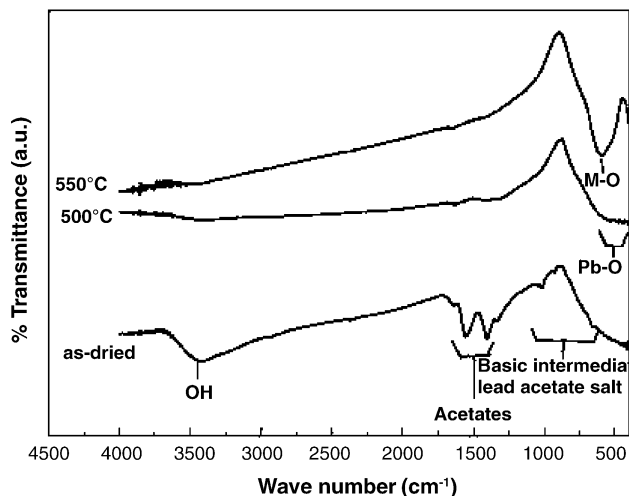


Fig. 3. FT-IR spectra of H.T. powders heated at various temperatures for 30 min.

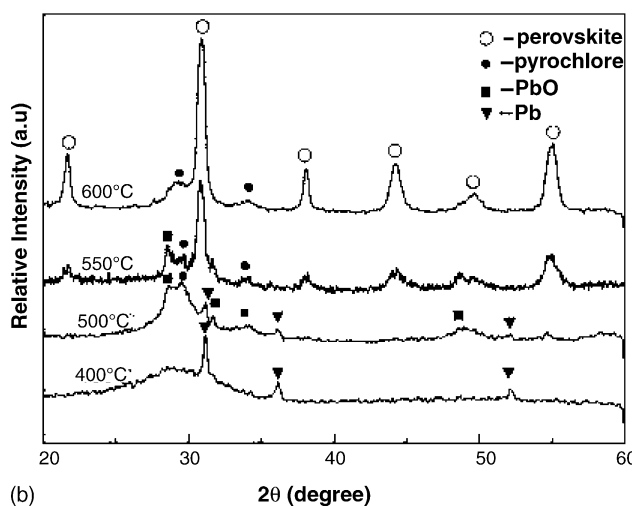
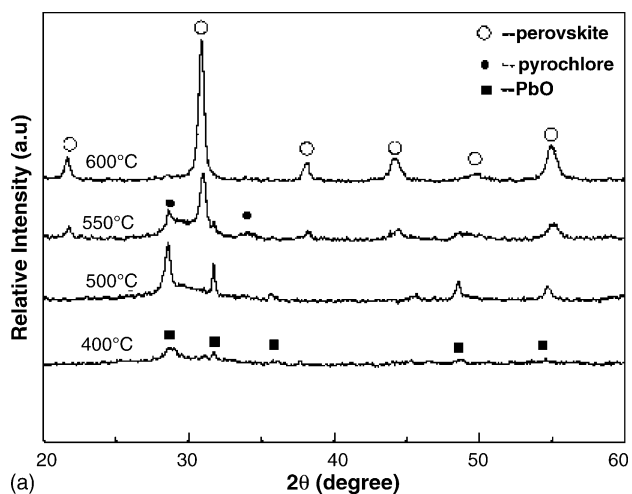


Fig. 4. XRD patterns of: (a) H.T. and (b) L.T. powders calcined at various temperatures for 30 min.

Fig. 1(b) reveals the TGA result of the H.T. and L.T. dried gels. In region I, the loss percentage of the H.T. and L.T. dried gels are similar (about 5.804 and 5.091%). As discussed above, the decomposition reaction of the anhydrous lead acetate occurred in the region II between 200 and 400 °C. In the early stage from 200 to 300 °C for region II, the loss percentage of the H.T. dried gels (14.909%) is obviously less than the L.T. (20.339%). It is caused by the anhydrous lead acetate partially decomposed by the preheating process at 300 °C for 1 h for the H.T. ones. The intermediate basic acetate salt decomposed and the PbO phase formed in the post stage of region II and the loss percentage of the H.T. dried gels (5%) is also less than the L.T. ones (6.251%). With the exception that the total weight loss of the H.T. dried gels of 25% is less than the L.T. ones of 32%, indicating higher PZT contents in the H.T. dried gels. It has been reported by Polli [24] that the powders with pre-pyrolysis would have higher PZT contents. With respect to color, the initial L.T. dried gels are black, suggesting the presence of carbonaceous material. The carbonaceous species could provide a local, low oxygen partial pressure during pyrolysis [24], which will lead to the Pb-partitioning. By contrast, the H.T. gels with fewer carbonaceous materials can avoid the Pb-partitioning and the final PZT contents become higher.

Fig. 2 presents the various heating rates of the DSC curve for the H.T. and L.T. dried gels. The dominant reactions denoted A–E peaks are the same as Fig. 1. It is well known that as the heating rate increases, the peaks shift to the higher temperatures [25]. According to the Kissinger's formula [27,28], the activation energies can be estimated. The activation energies (E_a) for various reactions were calculated from the linear regression of the Kissinger's formula, as shown in equation (1), when the heating rates were 2.5, 5, 10 and 20 °C/min [27,28],

$$\frac{d\left(\ln \frac{\alpha}{T_m}\right)}{d\left(\frac{1}{T_m}\right)} = -\frac{E_a}{R} \quad (1)$$

where, α is the heating rate (°C/min), T_m the absolute temperature (K) of the DSC curve and R represents the gas constant, 8.314 J mol⁻¹ K⁻¹. Following the Kissinger's method, the activation energies were calculated from the slope of the plot of $\ln(\alpha/T_m)$ and $(1/T_m)$. Table 1 lists the activation energies for the reactions A–E in Figs. 1 and 2. Peak D is responsible for the formation of the cubic pyrochlore phase. The data shows that the activation energy of the pyrochlore phase formation is similar for the H.T. and L.T. dried gels. Peak E is assigned as the formation of the dominant PZT perovskite phase. The activation energy for the H.T. dried gels is significantly lower than L.T. dried gels. It means that the H.T. dried gels transform to the perovskite PZT phase easily and will have higher proportion of the PZT phase.

From the DSC curves in Fig. 1, both the H.T. and L.T. dried gels decomposed from the anhydrous lead acetate to the PbO phase. However, Table 1 does not list the activa-

Table 1
Activation energies of various reactions for H.T. and L.T. dried gels

Reactions	Reactions	E_a of H.T. dried gel (kJ mol ⁻¹)	E_a of L.T. dried gel (kJ mol ⁻¹)
(A) The decomposition of acetate groups	$\text{Pb}(\text{CH}_3\text{COO})_2 \rightarrow \text{Pb}(\text{CH}_3\text{COO})_2 \cdot \text{PbO} \rightarrow \text{Pb}(\text{CH}_3\text{COO})_2 \cdot 2\text{PbO}$	24.9 ± 1.9	29.8 ± 1.7
(B) The decomposition of acetate groups	$\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 2\text{PbO} \rightarrow \text{PbO}_{1-x}(\text{CO}_3)_x$	56.2 ± 2.7	32.9 ± 1.9
(C) The formation of lead oxide	$\text{PbO}_{1-x}(\text{CO}_3)_x \rightarrow \text{PbO}$	210.0 ± 7.4	^a
(D) The formation of pyrochlore phase	–	351.4 ± 19.5	345.3 ± 24.2
(E) The formation of perovskite phase	–	424.5 ± 23.6	591.3 ± 41.3

^a Accompany reaction of $2\text{PbO} + \text{C} \rightarrow 2\text{Pb} + \text{CO}_2$ occurs at this reaction stage.

tion energy of peak C of the L.T. gels. The L.T. dried gels with higher residual carbon content will lead to the reduction of the PbO to element Pb and accompany reaction of $2\text{PbO} + \text{C} \rightarrow 2\text{Pb} + \text{CO}_2$ occurs at this reaction stage.

The FT-IR spectrum of the H.T. dried gels heated at different temperature for 30 min is shown in Fig. 3. The absorption band at 3400 cm⁻¹ corresponds to the stretching of –OH group [26]. Peaks around 1640 and 1315 cm⁻¹ are corresponding to free acetic acid or unidentate acetate [14]. There are two absorption bands at 1420 and 1560 cm⁻¹ which are attributed to the symmetric and asymmetric –COO⁻ stretching modes of the acetate groups [18]. The separation wave number between those two stretching modes ($\Delta\nu$) is a characteristic value, depending on the way carboxylate binds to the metal. If the $\Delta\nu$ value is less than 80 cm⁻¹, acetate is typically a cheating bidentate ligand. Otherwise, as the $\Delta\nu$ value is higher than 160 cm⁻¹, acetate is typically a bridging bidentate ligand [6]. The peaks around 1000 cm⁻¹ indicate that carbonate presents in the dried gels. It is interesting to note that due to the PZT, solution was heated at the temperature higher than the lead acetate decomposition temperature, the peaks defined as the basic intermediate acetate salt occur at 1050, 1020, 940, 930, 860, 666 and 620 cm⁻¹. Moreover, most of lead acetate has been decomposed completely in the H.T. dried gels heated at 500 °C for 30 min. The same results can be proven by the disappearance of 1420 and 1560 cm⁻¹ peaks. On the other hand, the PbO peak appears at the frequency region of 300–500 cm⁻¹, which is in good agreement with the XRD result shown in Fig. 4. A sharp spectrum of 600 cm⁻¹ peak shows in the H.T. dried gels heated at 550 °C, that refers to the M–O bonding (M means the metal element) [26]. Therefore, the formation temperature of the perovskite PZT should be above than 550 °C, which is in agreement with the DSC result in Fig. 1. The tendency of the L.T. dried gels for the FT-IR spectrum is the same as the H.T. ones (not shown here).

Fig. 4(a) shows the XRD results of the H.T. dried gels heated at various temperatures for 30 min. At 400 and 500 °C for 30 min, the dominant phase is the PbO. With increasing the temperature from 400 to 500 °C, the intensity of the PbO phase increases. The results indicate that the crystallinity of the PbO phase is enhanced with the increasing of temperature. The XRD result is in agreement with the decomposition reaction of the anhydrous lead acetate to the PbO phase at 400 °C in the DSC result and also with the Pb–O bonding at 500 °C in the FT-IR spectrum. As the temperature increases

to 550 °C, the XRD peaks identified as the PZT phase and the pyrochlore phase appear at the same time. The XRD peaks confirm the reactions for the peaks D and E in the DSC result and the M–O bonding at 550 °C in the FT-IR spectrum. When the temperature increases to 600 °C, the proportion of the pyrochlore phase apparently decreases and the crystallinity of the perovskite phase crystallized more completely.

Fig. 4(b) demonstrates the XRD results of the L.T. dried gels heated at the same conditions. At 400 °C for 30 min, the Pb-partitioning occurs in the L.T. dried gels in contrast to the PbO phase in the H.T. ones at the same temperature. The reason for the Pb-partitioning is attributed to the carbonate—the reducing agent—in the dried gels, which will lead to the reduction of the PbO phase to element Pb. The Pb-partitioning destroys the homogeneous distribution of all compositions in the amorphous PZT powders. The insignificant peak C in DSC shown in Fig. 1 is caused both by the endothermic decomposition reaction ($\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 2\text{PbO}$ to PbO) and the exothermic replacement reaction ($2\text{PbO} + \text{C} \rightarrow 2\text{Pb} + \text{CO}_2$). For the L.T. dried gels, the vague peak C and the higher total weight loss ratio in the DSC/TGA analysis all serve as another evidence of the Pb-partitioning. As the temperature rises to 500 °C, the peaks of the PbO and pyrochlore appear and the intensity of element Pb decreases. It is suggested that the formation of the PbO phase came from the oxidation of Pb or the product of the final decomposition reaction of the anhydrous lead acetate. As temperature increases to 550 °C, it shows the same tendency as the H.T. dried gels. The perovskite phase presents at 550 °C and crystallizes more completely at 600 °C. However, the contents of the pyrochlore phase are higher than the H.T. dried gels at 600 °C. It is worth to be noted that whether the Pb or PbO phase appear or not, the perovskite phase will be always formed and the result is in agreement with the previous study [24]. However, in this study, the formation temperature (550 °C) for the perovskite phase is lower than the previous study (700 °C) [24]. It could be due to the effective removal of the organic residues in the PZT gels before calcinations.

The relative perovskite content at various temperatures can be estimated from the intensities of the perovskite (1 1 0) peak and pyrochlore (2 2 2) peak using the relation $I_{\text{pero}}(1\ 1\ 0)/(I_{\text{pero}}(1\ 1\ 0) + I_{\text{pyro}}(2\ 2\ 2))$ [6,9]. Fig. 5 displays evolution of the relative perovskite phase content of the H.T. and L.T. dried gels calcined at various temperatures for 30 min. As the temperature is below 500 °C, the perovskite content is too low to detect. When the temperature is above

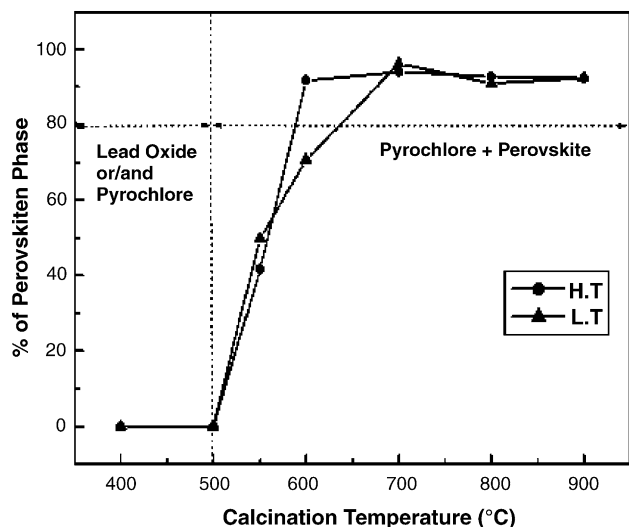


Fig. 5. Evolution of perovskite phase content of H.T. and L.T. powders calcined at various temperatures for 30 min.

550 °C, the relative contents of the perovskite phase increase obviously. It is reported that perovskite is formed at 700 °C [24], however, this study has efficiently decreased the PZT formation temperature to 550 °C. Comparing with the relative perovskite phase content at 600 °C for the H.T. and L.T. dried gels, the H.T. ones have higher proportion of the PZT phase. This is consistent with the lower activation energy of the PZT formation in the DSC result. As the temperature is higher than 600 °C, the relative PZT content does not change a lot. Therefore, the 600 °C is an adopt calcination temperature to obtain completely perovskite PZT phase transformation.

4. Conclusions

This study investigated the effects of different drying conditions for the PZT dried gels transformed to perovskite phase. From the thermal analyses, the PZT dried gels will transform to terminal perovskite phase and several intermediate products, including $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot \text{PbO}$, $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 2\text{PbO}$, $\text{PbO}_{1-x}(\text{CO}_3)_x$, PbO and pyrochlore were present in sequence. The weight loss of the H.T. dried gels in region II, in which organic residues decomposed, is lower than the L.T. ones. It reflects that the anhydrous lead acetate partially decomposed by the preheating process at 300 °C for 1 h for the H.T. dried gels. Moreover, the total weight loss of the H.T. dried gels is less than the L.T. ones, which indicate higher PZT contents in the H.T. dried gels. The activation energies for the various reactions were calculated from the linear regression of the Kissinger's formula and the activation energy of the perovskite formation for the H.T. dried gels is significantly lower than L.T. dried gels. It means that the H.T. dried gels transform to the perovskite PZT phase easily and will have higher proportion of the PZT

phase. From the FT-IR and XRD analyses, the L.T. dried gels contain more carbonaceous materials, which lead to the Pb-partitioning and the relative PZT perovskite contents become lower. On the other hand, by using the H.T. dried gels, it is successfully achieved to decrease the calcination temperature to 600 °C and to obtain fine-grained, high content of perovskite PZT phase.

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