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Application of lower temperature for crystallization of PbTiO3 nanopowders by the Sol-gel method

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The aim of this article is to decrease the crystallization temperature of the tetragonal perovskite $PbTiO_3$ nanopowders below the $PbTiO_3$ Curie temperature (~ 500 °C). At the beginning of our study, the calcination temperature was selected based on the thermal analysis of the $PbTiO_3$ gels, came out at 680 °C. However, detailed investigation of the thermal properties of the $PbTiO_3$ gel revealed possibility of the formation of single tetragonal perovskite phase at lower temperatures. Pb-partitioning phenomenon (section 3.2) was investigated in detail in PbTiO3 nanopowders in order to reach good crystallization below 500 °C. Both X-Ray diffraction and transmission electron microscopy investigations showed that well crystalline pure phase $PbTiO_3$ nanopowders have been synthesized after calcination of the $PbTiO_3$ gel at 460 °C, which is quite close to the Curie temperature of the $PbTiO_3$ nanoparticles. To improve crystallization of the samples prepared at 460 °C, the effects of the heat treatment parameters and Pb content on gel crystallization were investigated in detail.

Key words: Nanopowders, $PbTiO_3$, Sol-gel Preparation, Crystallization.

Introduction

Lead titanate or $PbTiO_3$, with the tetragonal perovskite structure, is a well-known piezoelectric and ferroelectric material with good ferroelectric properties. This material exhibits a wide spectrum of functional properties such as switchable polarization, piezoelectricity, high non-linear optical activity, pyroelectricity and high dielectric behavior [1, 2]. PbTiO3 nanoparticles are in focus of investigations, both theoretically and experimentally; it is already shown theoretically that ferroelectricity can be sustained in some PbTiO3 nanoparticles of only a few lattice constants in size [3], and experiment shows that PbTiO3 nanodots with diameters less than 10 nm exhibit good ferroelectric properties [4].

Similar to other PbO-based ferroelectrics, PbTiO3 has several technical problems which limit its fabrication and application. Since PbO is a toxic volatile material, its evaporation at high temperatures produces porosity in the synthesized material and makes poisonous productions or releases toxic Pb compounds, which poses a hazard for the environment. A specific drawback of PbTiO3 is its large lattice distortion during cubic- tetragonal phase transition around 500 °C. It is difficult to fabricate high quality PbTiO3 ceramics above 500 °C because of this lattice distortion results in large volume change, upon cooling, around this temperature which leads to internal stresses in the samples. For this reason, bulk sintered PbTiO3 ceramics are fragile and may disintegrate into powder at room temperature due to mechanical breakdown [5]. For several decades, researchers have attempted fabricating dense modified PbTiO3 ceramics by adding suitable additives. However, it is known that most of these additives change the ferroelectric properties of PbTiO3 [6, 7].

Some authors have already reported various methods for the synthesis of PbTiO3 nanopowders [8-13] among which, the sol-gel methods have the advantages of being cheap and simple and precise control of the composition. However, to the best of our knowledge, the entire crystallization of the tetragonal perovskite $PbTiO_3$ nanopowder by the sol-gel method requires heat treatment of the PbTiO3 gel between 650 °C and 700 °C [8, 14, 15, 13], which is disadvantageous because it results in an increase of the crystallite size as well as an increase of Pb evaporation. In addition, PbTiO3 nanostructures which are sintered at these temperatures (650-700 °C) face up to the large lattice distortion which occurs about 500 °C.

We have attempted decreasing the crystallization temperature of PbTiO3 nanopowders produced by sol-gel processing. We have investigated the Pb-partitioning phenomenon (section 3.2) in more detail in PbTiO3 nanopowders in order to reach the crystallization below 500 °C. Our approach has the advantage of not suffering from the disadvantages attributed to the conventional sol-gel processing of Pb-based ferroelectric materials.

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Experimental

Sol-gel processing

Stabilized $PbTiO_3$ precursor sols were prepared through chemical modification of the organometallic precursors of titanium by acetic acid. Details of this method was already reported elsewhere [13]. Typically, in order to prepare the $Pb_{1.05}TiO_3$ precursor sol, 27.95gr lead acetate trihydrate (99.5% purity, Merck) was dissolved in 24.04 ml pure glacial acetic acid. Then, the prepared solution was dehydrated at 110 °C for 15 min and cooled down to room temperature. After cooling down, 23.25 ml titanium butoxide (98% purity, Merck) was added gradually, drop by drop, to the solution. For 15min, this solution was stirred at room temperature, and then, a mixture of 12.01 ml de-ionized water and 33.45 ml ethanol (99.5% purity, Merck) was added to cause hydrolysis and prevent fast gelation of the prepared sol. Then, 4.13 ml Ethylene glycol (99% purity, Merck) and 6.92 ml acetyl acetone (99% purity, Merck) were added to enhance viscosity and stability of the final precursor solution. The prepared sols were heated, along with continuous stirring, to obtain the $PbTiO_3$ gels, and the prepared gel was subsequently dried at 100 °C for 10 hours.

Preparation and characterization of PbTiO3 nanopowders

The proper gel calcination temperature for the growth of the perovskite tetragonal structure in the $PbTiO_3$ powder was selected based on simultaneous thermal analysis (TG/DTA) of the prepared gel. Thermal analysis was carried out on a Perkin Elmer model Pyris diamond S(II) thermal analyzer with the rating of 10 °C/min. The prepared $PbTiO_3$ nanopowders were investigated using a transmission electron microscope (TEM) system model Philips EM208S. The prepared nanopowders were also analyzed by X-Ray diffraction (XRD) method, using Cu Kα radiation, employing a Bruker-d8 advance model. The obtained XRD data were analyzed to identify the crystal structure of the calcinated $PbTiO_3$ nanopowders and calculate semi-quantitatively the crystallized percentage of the powder in order to evaluate the best heat treatment condition for preparing well crystallized homogenous $PbTiO_3$ nanopowders. XRD data were recorded using similar angular and time steps and reported as measured (i.e., no data normalization was performed).

Results and Discussion

Various characterization techniques were used in order to demonstrate crystallization of our $PbTiO_3$ nanopowder samples at 460 °C and or optimize the processing parameters. First, thermal properties of the precursor gel were investigated in detail.

Detailed investigation of thermal properties of our $PbTiO_3$ gel

Fig. 1 shows the results of the thermal analysis of our $Pb_{1.05}TiO_3$ gel sample. As it is seen, at the beginning of the DTA graph, a broad exothermic region is observed below 280 °C (Point O). This exothermic region is accompanied by a steep decrease of the weight in the thermal gravimetry (TG) plot (the AB region in Fig. 1). It is already reported that this exothermic region is due to alcohol removal [16].

An exothermic region is observed in the DTA graph below 320 °C (Point P), and an endothermic region is located around 330 °C (Point Q), which the latter is accompanied by a steep decrease of the weight in the TG plot (BC region, Fig. 1). Then a very broad weak exothermic region is observed below 400 °C (Point R). Weight loss is observed within the 330-400 °C range, but, rate of the weight reduction rate decreases gradually in this region (BC region, Fig. 1), so that, the weight loss in this region may be due to the endothermic region about 330 °C (Point Q). Hence, the 330-400 °C range could be considered as the crystallization range for the perovskite or an intermediate $PbTiO_3$ phase.

There is a rather sharp exothermic peak around 460 °C (Point S), which is related to the removal of the rest of the left organic materials as well as the structural water. Later, a wide exothermic peak was seen at 680 °C in the DTA graph (Point S). No weight loss was observed in the TG graph around this temperature (the DE region, Fig. 1). Therefore, it was concluded that the mentioned peak (680 °C) is due to crystallization of the perovskite $PbTiO_3$ phase. Based on the latter results, heat treatment at 680 °C was successfully tested for the preparation of $PbTiO_3$ nanopowders in our previous work [13]. But, here, in order to identify which phase could crystallize in the 330-400 °C temperature range and decrease the crystallization temperature of the tetragonal perovskite $PbTiO_3$ nanopowders below 500 °C, the following

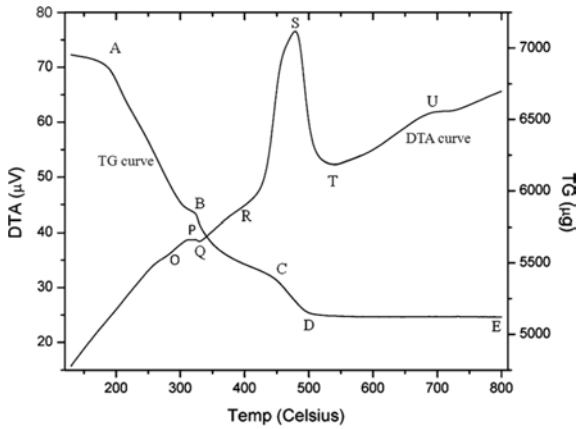

Fig. 1. The simultaneous thermal analysis (TG/DTA) of the dried $PbTiO_3$ gel.

investigations were carried out at both 460 °C and 680 °C. Pb-partitioning was investigated in PbTiO3 nanopowders produced by sol-gel processing, and the effect of the heat treatment parameters on the perovskite phase crystallization was studied.

Pb-partitioning phenomenon in the PbTiO3 nanopowders

In the first part of this study, Pb-partitioning was investigated in our PbTiO3 nanopowders in order to improve crystallization below 500 °C. Different extra Pb contents were added to the $PbTiO_3$ sols. So that, it was expected that Pb-partitioning would be observed in some $PbTiO_3$ nanopowder samples, after heat treatment at 680 °C; because Pb-partitioning (formation of Pb element during heat treatment) happens in varying amount of containing excess Pb in the PbO-based samples during decomposition of the organic materials. Presence of the carbonaceous species provides a reducing atmosphere locally and may reduce PbO into Pb. This phenomenon delays crystallization of the perovskite phase and leaves toxic PbO compounds in the samples.

Heat treated at 680 °C for 6 hours, the produced $PbTiO_3$ powders having extra Pb contents of 0%, 5% and 10% (Samples A-C, in table 1) were analyzed by XRD (Fig. 2). It is observed in Fig. 2 that the tetragonal perovskite $PbTiO_3$ phase is formed in all samples after the aforementioned heat treatment. However, the calculated crystalline percentage is different in the prepared samples. In addition, there are some peaks associated with the undesirable PbO phase present in the XRD pattern of the annealed $PbTiO_3$ gels with 5% and 10% (sample A and B, Table I) extra Pb content. The undesirable PbO phase has been removed in Fig. 2-a, but the crystallinity of the sample, percentage of the tetragonal perovskite $PbTiO_3$ phase, is the least among the analyzed samples, for the sample containing 0% extra Pb (sample C, Table I). XRD pattern of the annealed $PbTiO_3$ gel with 5% extra Pb is shown in Fig. 2-b. This figure indicates clearly that some amount of the undesired PbO phase exists in the XRD pattern of the sample containing 5% extra Pb (sample B, Table I), but the crystallization is more than the sample containing 0% extra Pb (sample C, Table I). Moreover, less amount of the undesired PbO phase exists in the XRD pattern, but the crystalline intensity is also less than the sample containing 10% extra lead; see Fig. 2-c (sample A, Table I).

It is shown here that Pb content has a key contribution in the crystallization of the PbTiO3 tetragonal perovskite phase. Samples having extra Pb content of 5% ($Pb_{1.05}TiO_3$) were selected for the rest of the current investigation.

Table 1. Pb content and preparation conditions of different samples which were examined in this study.

Nanopowder samples	Pb Content	Firing temperature (°C)	Firing time (hours)	Heating rate (°C/min)	Percentage of crystallization (%)
A	1.10	680	6	20	81.3
B	1.05	680	6	20	72.6
C	1.00	680	6	20	67.5
D	1.05	680	4	20	73.5
E	1.05	680	2	20	78.5
F	1.05	460	2	20	47.5
G	1.05	460	2	10	Not calculated

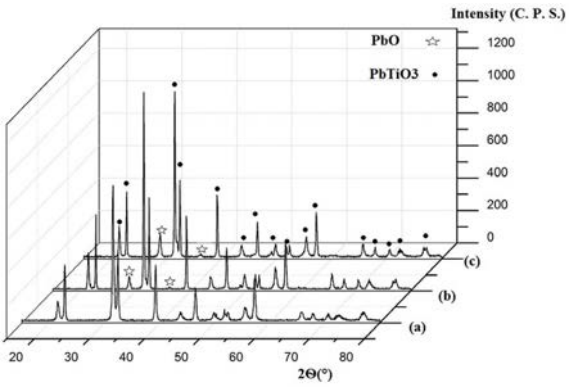

Fig. 2. Pb-partitioning results: XRD patterns of the $PbTiO_3$ gels with the extra Pb contents of a) 0%, b)5%, and c)10% after annealing at 680 °C for 6hours.

Effect of calcination time

The next parameter which was studied here, in order to obtain crystallization of the tetragonal perovskite $PbTiO_3$ nanopowders below 500 °C, was the period of the final calcination step.

Figs. 3a and 3b shows the effect of the calcination time on the phase structure of the $Pb_{1.05}TiO_3$ sample. The XRD powder samples were prepared at 680°C by applying different heat treatment time of 2, 4 and 6 hours (Samples E, D and B in table 1, respectively). In both Fig. 3b and Fig. 3c, the intensity of the peak associated with the (101) plane has increased compared to Fig. 3a. However, other diffraction peaks have larger intensities in Fig. 3a.

The crystalline percentage of the prepared powders was also calculated semi-quantitatively through analyzing the measured XRD data, as reported in table 1. It is interesting to note that increasing heat treating time at 680°C for 2 to 6 hours has conversely affected the crystalline percentage of the prepared lead titanate powders (as observed in table 1). Similar effects were also observed in other samples. The reason may be PbO evaporation during the heat treatment stage, as confirmed by the large variation of the XRD peaks due to PbO (Fig. 3 a-c). Since PbO content has a key contribution in the crystallization of the $PbTiO_3$ tetragonal perovskite phase (section 3.2), PbO evaporation results in lower $PbTiO_3$ crystallization. Accordingly, to improve crystallization of

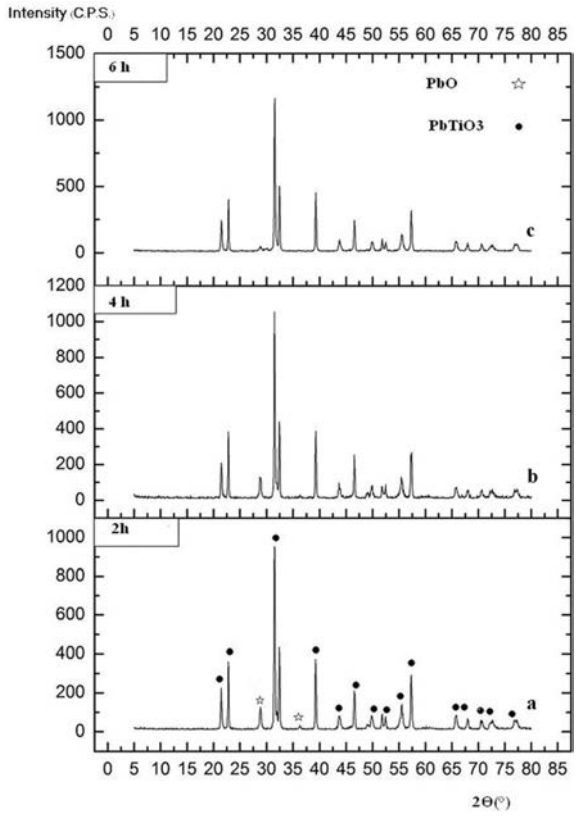

Fig. 3. Effect of the calcination time: XRD patterns of the $PbTiO_3$ nanopowders with the extra Pb content of 5% prepared at 680 ºC for a) 2 hours, b) 4 hours, c) 6 hours.

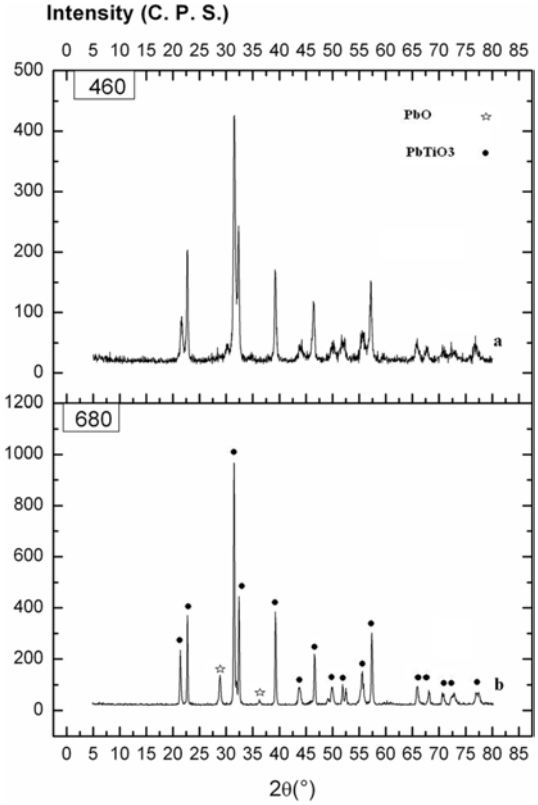

Fig. 4. Effect of firing temperature on crystallization of $Pb_{1.05}TiO_3$ powder at a) 460 ºC b) 680 ºC.

the tetragonal perovskite $PbTiO_3$ nanopowders below 500 ºC, the significance of utilizing an optimized calcination time (not a longer one) can be recognized from our results.

Crystallization of PbTiO3 nanopowders at lower temperatures

In order to obtain crystalline PbTiO3 nanopowders at lower temperatures, the effect of the firing temperature was also investigated. Figs. 4-a and 4-b show the XRD patterns of the $PbTiO_3$ gels, with 5% extra Pb content, which are heat treated at 460 ºC and 680 ºC, respectively. Both samples are heated with a similar heating rate of 20 ºC/min. Crystallization of the tetragonal perovskite $PbTiO_3$ phase was demonstrated by XRD analysis, see Fig. 4-a (sample F, Table I) and Fig. 4-b (sample E, Table I). Our XRD results clearly show that the first temperature for starting the crystallization of lead titanate occurs below 460 ºC.

It should be noted that we could not get rid of the peaks due to PbO in the samples heat treated at 680 ºC for 2 hours which result in fabrication of poison $PbTiO_3$ productions, see Figs. 2-a and 4-b. However, the intensity of the PbO peaks decreased drastically after heat treatment at 460 ºC. Our results confirm the beneficial effect of the lower temperature crystallization of PbTiO3 nanopowders for the environment.

It is found here that it is possible to minimize the undesirable Pb-partitioning phenomenon in $PbTiO_3$ nanopowders and simultaneously improve crystallization of the PbTiO3 tetragonal perovskite phase at lower temperatures.

Effect of the heating rate

Our thermal analysis results may indicate complete removal of the organics about 460 ºC. However, for entire crystallization of PbTiO3 nanopowders at this temperature it is necessary to optimize the heat treatment parameters. Hence, in order to optimize the heat treatment parameters, in the fourth set of our experiments, the effects of the heating rate on the crystallization of the tetragonal perovskite PbTiO3 and the final phase composition of the prepared nanopowders were studied. Figs. 5-a and 5-b show the XRD patterns of the $Pb_{1.05}TiO_3$ gels, which are heated at 460 ºC with the rate of 10 ºC/min (sample G, table 1) and 20 ºC/min (sample F, table 1), respectively. As it is seen in table 1, the sample which is heat treated at a heating rate of 20 ºC/min exhibits better crystallization of tetragonal $PbTiO_3$. On the other hand, the sample heat treated with the 10 ºC/min heating rate exhibit formation of more undesirable PbO phase and less crystallization of PbTiO3 perovskite phase. This indicates the existence of more organic components due to less decomposition of the organics in the intermediate temperatures, which results in Pb-partitioning (Fig. 5-a, sample G in table 1).

Hence, a 20 ºC/min heating rate was selected in the rest of our study for better crystallization and lower Pb-partitioning.

It is notable that, according our XRD results, the $Pb_{1.00}TiO_3$ gel sample (gel containing no extra Pb content) shows crystallization of single phase tetragonal $PbTiO_3$ only after heat treatment at 680 ºC (Fig. 2a). This temperature is the same as our previous studies. However, by studying the Pb-partitioning in this material and optimizing the Pb content and the heat treatment parameters, XRD investigations confirmed that the researchers here have obtained single phase crystallization of lead titanate nanopowders by sol-gel method about 460 ºC which is a much lower than the temperature range 650-700 ºC as reported by others [8, 14, 15].

TEM Analysis

TEM microstructural and electron diffraction analyses were performed in order to investigate size, morphology and phase composition of the prepared $PbTiO_3$ nanoparticles.

To confirm our XRD results, the $Pb_{1.05}TiO_3$ powder, prepared with the optimum parameters; heat treated at 460 ºC for 2 hours with a 20 ºC/min heating rate, was selected for our TEM analyses. As shown in Fig. 6, a uniform morphology is achieved in $PbTiO_3$ nanoparticles heat treated at 460 ºC, which indicates that our method has been a suitable synthesis one.

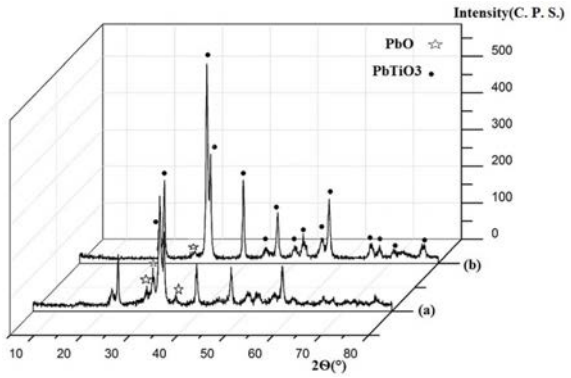

Fig. 5. Effect of the heating rate: XRD patterns of the $PbTiO_3$ nanopowders containing 5% extra Pb prepared at 460 ºC for 2 hours, using a) 10 ºC/min heating rate b) 20 ºC/min heating rate.

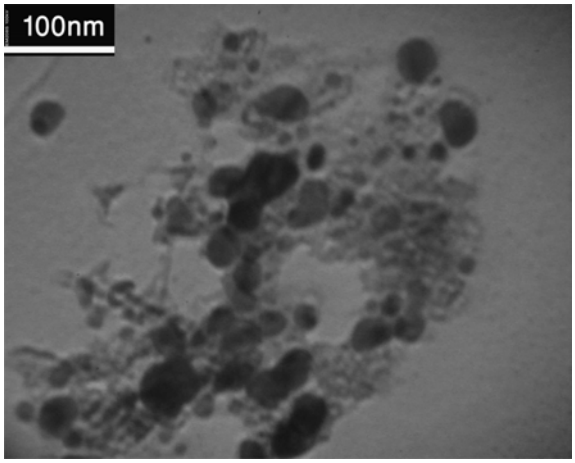

Fig. 6. The TEM image of the $PbTiO_3$ nanoparticles in our optimized sample, the sample prepared at 460 ºC for 2 hours.

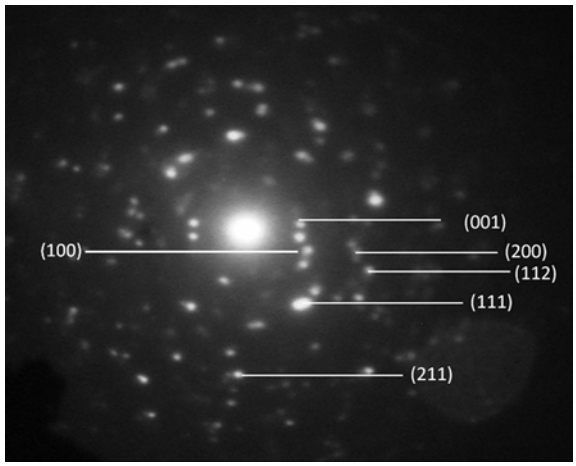

Fig. 7. The electron diffraction pattern of the prepared nanoparticles in Figure 6 showing single phase crystallization of $PbTiO_3$ tetragonal perovskite phase.

Fig. 7 shows the diffraction pattern of the $PbTiO_3$ nanoparticles in Fig. 6. All the diffraction points correspond with the tetragonal perovskite phase according to the JCPDS card No. 6-452. As shown in this figure, single phase tetragonal perovskite $PbTiO_3$ nanoparticles are formed, which confirms that low temperature single phase crystallization of $PbTiO_3$ has occurred at 460 ºC whereas crystallization of $PbTiO_3$ has already been reported above 650 ºC [8, 14, 15].

The diffraction points in this figure clearly show Bragg angle splitting. This angular splitting indicates formation of the tetragonal perovskite structure, which is confirmed with peak splitting in XRD results; see for example, splitting of the (001) and (100) patterns in Fig. 7 which matches splitting of the 32 º peaks in XRD patterns in Figs. 3-5. Therefore, well crystalline tetragonal perovskite PbTiO3 nanoparticles are synthesized here at 460 ºC (Fig. 7), while they are already prepared at 680 ºC [13].

Advantages of our Method

Our XRD results confirm formation of single phase tetragonal perovskite PbTiO3 nanopowders below 500°C. Therefore, the prepared $PbTiO_3$ nanopowders avoid large lattice distortion around 500°C and may avoid formation of poison productions or release of toxic Pb compounds into the environment (section 3.4). This is promising for future applications.

As shown by our TEM micrographs, the prepared $PbTiO_3$ nanoparticles mostly have dimension of about 25 nm. Thus, according to the empirical expression presented by Ishikawa and coworkers[17], they have a

Curie temperature of above 450 °C. Our results indicate complete removal of the organics about 460 °C. However, by using our method, pure tetragonal perovskite phase $PbTiO_3$ phase forms below 460 °C. Therefore, pure tetragonal perovskite phase $PbTiO_3$ nanostructures may be densified below 460 °C. As a result, the $PbTiO_3$ nanostructures which are prepared by this way can also avoid the large lattice distortion due to cubic-tetragonal phase transformation around 500 °C. However, further development of such a desirable lower temperature ceramic processing needs to systematic supplementary experiments.

Our results indicate significance of utilizing an optimized calcination time in order to improve crystallization of the tetragonal perovskite $PbTiO_3$ nanopowders. This can help fabricating $PbTiO_3$ nanopowders cost effective; because table 1 shows that more energy consumption for the application of longer heat treatment procedures is not practically reasonable.

Many researchers have attempted lower temperature crystallization of $PbTiO_3$ nanopowders. Ishikawa and coworkers were prepared PbTiO3 nanoparticles via the sol-gel process using metal alkoxide precursors[8]. They claimed that crystallization of the amorphous PbTiO3 gel may occur below 460 °C. However, they did not present any experimental evidence. But, our research work indicates that crystallization of the amorphous PbTiO3 gel into the tetragonal perovskite phase definitely occurs below 460 °C by selecting a convenient Pb percentage and an optimized heat treatment process.

Kakihana and coworkers reported crystallization of $PbTiO_3$ nanopowders at 400 °C [18]. However, their method is quite different from us. It should be noted that their synthesis method is mostly applicable for powder preparation. But, our alkoxide-based method is more general than their method, because our method is applicable for the synthesis of various nanostructures (thin films, nanodots, nanorods, etc).

Conclusions

Crystallization temperature is a vital problem in nanotechnology. The researchers here have obtained single phase crystallization of lead titanate nanopowders by the sol-gel method at 460 °C which is a much lower temperature than the 650-700 °C range, as reported by others. Crystallization at 460 °C decreases Pb evaporation efficiently during the heat treatment, which can minimize release of toxic Pb compounds in the environment and can protect the stoichiometric ratio of Pb/Ti.

Our XRD investigations on the calcinated nanopowders showed that the complete crystallization of the amorphous $PbTiO_3$ into the $PbTiO_3$ perovskite structure would be possible only after optimizing the heat treatment condition and investigating the effect of Pb content, as performed here. Thus, an optimized calcination time, not a longer one, is necessary to improve crystallization of the tetragonal perovskite $PbTiO_3$ nanopowders (section 3-3). These results can help fabricating $PbTiO_3$ nanopowders cost effective (section 4).

Our TEM and electron diffraction investigations showed that well crystalline $PbTiO_3$ nanoparticles with a rather uniform morphology can be produced at 460 °C whereas formation of such nanoparticles have already been reported above 650 °C. Therefore, in the future, by using our method and performing supplementary experiments; the $PbTiO_3$ nanostructures may avoid the large lattice distortion due to cubic- tetragonal phase transformation.

Our results demonstrated the essential importance of the lower temperature crystallization of $PbTiO_3$ nanopowders. To the best of our knowledge, our article is the first one which presents experimental evidence on effective crystallization of the amorphous $PbTiO_3$ gel into the perovskite phase below 460 °C, for the $PbTiO_3$ nanoparticles produced by the alkoxide-based sol-gel method. This issue has been attempted by other researchers too. But, no evidence has been already presented. Crystallization of $PbTiO_3$ nanopowders at 400 °C is already reported for the polymerized complex synthesis method, which is mostly applicable for powder preparation. But, alkoxide-based method is more general, because this method can be applied for the fabrication of different nanostructures (nanowires, nanotubes, etc).

Acknowledgments

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