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Novel Solid-State Reaction Route to Synthesize $Pb(Mg_{1/3}Nb_{2/3})O_3-PbTiO_3$ Ceramics with a Pure Perovskite Phase

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Development of electronic devices such as sensors, actuators, and capacitors requires materials with excellent electromechanical properties, as well as a reliable processing route.[1] Specifically, low cost and low temperature processing of the materials is necessary for large-scale applications. Among the various methods for the synthesis of ceramic materials, the conventional solid-state reaction process is most widely used because of the simple procedures and low cost. Ferroelectric materials such as $Pb(Zr, Ti)O_3$ (PZT)[2] and $BaTiO_3$ (BT)[3] with a perovskite structure can be synthesized successfully with this method. However, this method failed in preparing the relaxor-type ferroelectrics because unwanted pyrochlore phases are inevitably formed and difficult to remove.[4,5] The relaxor-type ferroelectric systems such as $Pb(Mg_{1/3}Nb_{2/3})-PbTiO_3$ (PMN-PT), $Pb(Ni_{1/3}Nb_{2/3})-PbTiO_3$ (PNN-PT), and $Pb(Zn_{1/3}Nb_{2/3})-PbTiO_3$ (PZN-PT) have attracted much attention as a result of their excellent properties caused by the coexistence of two phases at the morphotropic phase boundary (MPB).[6,7]

To avoid the formation of pyrochlore phases and to obtain pure perovskite phase in the synthesis of the relaxor ferroelectrics, a two-step calcination technique called the columbite method was developed by Swartz and Shrout.[8] In this method, the columbite ($MgNb_2O_6$) is first synthesized at 1000 °C and then reacts with PbO and TiO_2 at 900 °C to form perovskite phase. There are several other processing methods which use liquid precursors as starting materials. Pioneered by Pechini in the 1960s,[9] polymer species was added to the liquid precursor solution to form the polymer−cation complexes which aid the crystallization. In our previous work, poly(ethylene glycol) (PEG) was used to modify the PZN-based precursor in the sol−gel method. It was found that PEG promoted the formation of the perovskite phase and supressed the formation of pyrochlore phase in the PZN-PT thin films.[10] However, these liquid precursor methods are not suitable for mass production in thick films or ceramics.

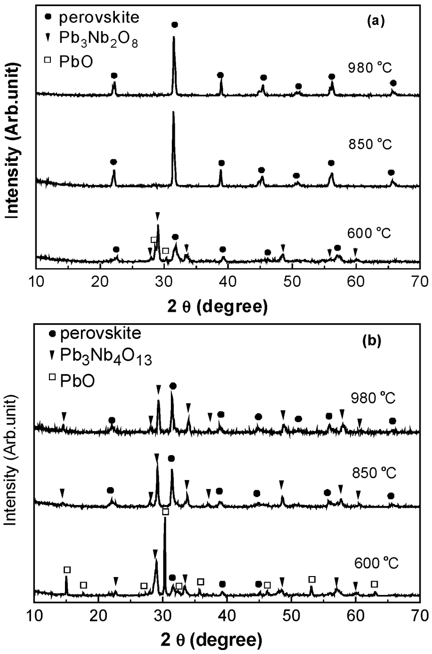

Figure 1. XRD patterns of the PMN-PT powders derived from (a) the oxide precursor mixed with PEG200 and (b) the oxide precursor without PEG. Powders were calcined at different temperatures for 2 h.

Although polymer species are commonly used in sol−gel processes,[9−11] no attempts have been made to use polymers in the solid-state reaction to synthesize ceramics. It is well-known that most polymers or oligomers decompose at a temperature (~200−400 °C) much lower than the reaction temperature (>600 °C) of oxides. However, results in this study demonstrate that, once mixed with the precursor oxides, the polymers tend to interact with the oxides. As a result, decomposition of the polymers is retarded to a higher temperature which consequently affects the phase formation.

In the present work, by simply introducing PEG to the mixture of PbO, MgO, Nb_2O_5, and TiO_2, we have successfully synthesized perovskite PMN-PT powders at relatively low temperatures with a one-time mixing solid-state reaction. PEG with a molecular weight of 200 (PEG200) was employed. The $(1-x)$PMN-xPT with a MPB compostion at $x = 0.35$ was synthesized. The method reported in this communication eliminates the step to form the columbite phase and makes it possible to synthesize the relaxor-type ferroelectrics through a simultaneous oxides mixing process. The role of PEG in the crystallization is investigated.

Both pyrochlore and perovskite phases are detected by X-ray diffraction (XRD) (Figure 1a) for the oxides mixed

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with PEG200 and calcined at 600 °C. PbO is nearly undectable, which means most of it has participated in the crystallization of perovskite or pyrochlore phase. Therefore, the pyrochlore phase appearing at 600 °C can be assigned to the lead-rich $Pb_3Nb_2O_8$, which will react with MgO at increased temperatures to form perovskite phase. As a result, the powder calcined at 850 °C exhibits nearly single perovskite phase which is stable up to 980 °C. The calculated lattice constant of the psudo-cubic perovsktie phase formed at 600 °C is 3.93 Å, which is close to that of pure $PbTiO_3$ (3.89 Å). The lattice constant of the powders calcined at 850 °C is 4.00 Å and close to that of PMN (4.04 Å). Changes in the lattice constant indicate that with the increase of temperature, more MgO and Nb_2O_5 are involved in the formation of perovskite PMN-PT and thus enlarge the lattice.

On the contrary, for the oxide precursor without PEG addition, a large amount of PbO exists in the sample calcined at 600 °C, as shown in Figure 1(b). The pyrochlore phase is assigned to the lead-deficient $Pb_3Nb_4O_{13}$, which is confirmed by the energy dispersive X-ray (EDX) analyzer analysis (not shown). The intensity of the pyrochlore phase does not change much when the sample is calcined at 850 °C, although PbO is not detected. In contrast, the intensity of the perovskite phase increases substantially. The results indicate that with the increase of calcination temperature, PbO is involved in the formation of perovskite phase mainly by reacting with TiO_2. On the other hand, the pyrochlore phase $Pb_3Nb_4O_{13}$ formed at 600 °C remains unchanged with increasing temperature up to 980 °C. Bhat et al.[12] and Lejeune and Boilot[13] also reported that $Pb_3Nb_4O_{13}$ was difficult to convert to the perovskite or other type of pyrochlore phases once it was formed. The reason is that, compared with the perovskite phase, $Pb_3Nb_4O_{13}$ is B-site rich and it is difficult to enter Mg into the B-site to form perovskite structure.

The above results indicate that PEG has interacted with the oxide precursor in a way aiding the formation of the perovskite phase. As shown by the XRD results, the amount of PbO is largely reduced at 600 °C when PEG is added, which indicates that PbO participates in the crystallization at a low temperature with PEG present. The results from thermal analysis as discussed below confirm that the interaction occurs between PEG and PbO.

Thermogravimetry (TG) and differential scanning calorimetry (DSC) of the slurry mixed with PEG show curves different from that without PEG as indicated in Figure 2. Combustion of pure PEG has completed at 227 °C, corresponding to an exothermic valley at 210 °C in the DSC curve. The small valley at 256 °C in the DSC curve may correspond to the oxidation of the carbon residues by self-combustion. The two exothermic valleys shift to higher temperatures, that is, 254 °C and 294 °C, respectively, for PMN-PT with PEG200, which correspond to an initial weight loss in the region of ∼200−300 °C due to the decomposition of PEG chains. This phenomenon indicates that there are interactions between PEG and the oxide precursors which retard the decomposition of PEG. However, the PEG mixed with the oxides has not combusted completely even up to 300 °C. The weight loss at ∼300−460 °C is attributed to the combustion or oxidation of the broken chains connected to the oxides by a stronger bond. This process corresponds to a weak exothermic hump at 369 °C and a sharp exothermic valley at 437 °C in the DSC curve which ends at 500 °C. XRD results show that the precursor heated at 500 °C is a mixture of pyrochlore, perovskite phases, and other oxides, which indicates that the exothermic valley at ∼400−500 °C accompanies the crystallization process. The weight loss beginning at about 850 °C is caused by the vaporization of lead oxide. The broad valley in the temperature range of ∼600−1000 °C corresponds to the phase transition process, involving the transformation of pyrochlore to the perovskite phase. In contrast, for the oxide precursors without PEG, there is only a small weight loss between ∼321−347 °C, corresponding to the small valley at 344 °C in the DSC curve, which is caused by the release of carbon or hydroxyl attached to the oxides as impurities.

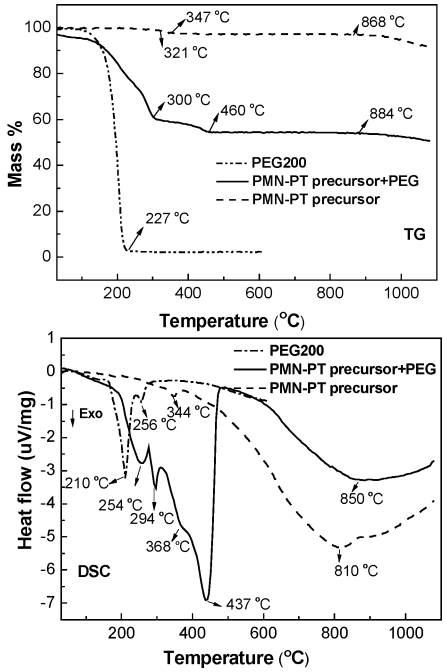

Figure 2. TG/DSC curves for pure PEG200, PMN-PT oxides precursor mixed with PEG200, and PMN-PT oxides precursor without PEG.

Thermal behavior of the PbO + PEG200 and MgO + Nb_2O_5 + TiO_2 + PEG200 (MNT + PEG) further confirms that the interaction happens between PbO and PEG, as indicated by Figure 3. Similar to the TG curve of PbO + MgO + Nb_2O_5 + TiO_2 + PEG200 (PMNT + PEG200) in Figure 2, decomposition of PEG in the PbO + PEG mixture is also retarded, and there is a step in the weight loss ranging ∼300−480 °C, indicating the combustion or oxidation of the broken chains connected to PbO by a stronger bond. In contrast, although there is also a minor retardation of PEG decomposition (250 °C compared to 227 °C of the pure PEG) in the curve of MNT + PEG, no prominent step is observed above 250 °C.

The above results demonstrate that interaction between PEG and PbO alters the reaction process of the crystallization during heat treatment. As a result of the interaction with PEG,

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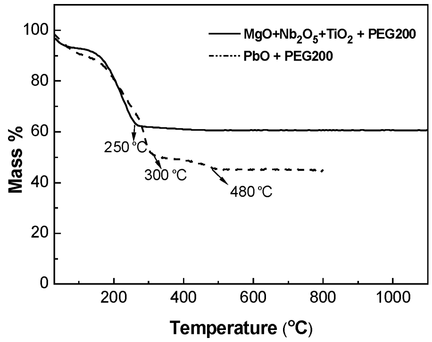

Figure 3. TG curves for the mixtures of PbO + PEG200 and MgO + Nb_2O_5 + TiO_2 + PEG200.

PbO particles are covered by a thin layer of PEG, and they remain stable up to 460 °C. With the decomposition of PEG, almost all the lead oxides take part in the crystallization process involving the formation of both perovskite and Pb-rich pyrochlore phase $Pb_3Nb_2O_8$. At elevated temperatures, it is easy for the Mg element to be incorporated into the Pb-rich pyrochlore to form the perovskite phase. In contrast, when PEG is absent, PbO is not activated so that the Pb-deficient pyrochlore such as $Pb_3Nb_4O_{13}$ tends to form which is difficult to incorporate with any more Mg element. The fact that MgO participates in the formation of perovskite phase at a higher temperature by incorporating into the Pb-rich pyrochlore was previously reported by Bhat et al.[12] and Lejeune and Boilot.[13]

Pyrochlore phases are common in the synthesis of Pb-containing and Bi-containing materials. Formation of the pyrochlore phases is attributed to the $6s^2$ lone pair in Pb^{2+} or Bi^{3+}, which has a stereochemical activity and tends to accommodate itself to an anion site, which leads to the formation of the pyrochlore phase.[14,15] In the PEG structure $OH-(CH_2CH_2O)n-H$, both of the ether oxygens $-O-$ and oxygens from $HO-$ behave as Lewis bases, which interact with PbO as electron donors. As a result, the lone $6s^2$ electron pair is repulsed to an inner level, thus losing its directional activity. This analysis is consistent with the study of Shimoni-Livny's group[16] on the stereochemical activity of the lone pair in divalent Pb compounds. Besides, when interacting with PEG, the environment of PbO is oxygen-rich. Therefore, formation of the cubic pyrochlore with oxygen vacancies such as $Pb_3Nb_4O_{13}$ is suppressed.

Development of the oxides mixed with PEG200 is examined with scanning electron microscopy (see Supporting Information). After the ball milling process, the oxides are wrapped in the PEG matrix. Uniformly sized powders are obtained when the mixture is heat-treated at 600 °C, a temperature where the pyrochlore and the perovskite phases coexist. The powders grow into larger perovkiste grains (~1−2 μm) after calcination at 850 °C. The powders with perovskite phase can be synthesized at 850 °C in this study, which is much simpler than the columbite method, and the temperature is even lower than in the sol−gel method (1040 °C).[17,18]

In conclusion, the PMN-PT powders with perovskite phase have been successfully synthesized by introducing PEG to the conventional solid-state reaction process. By interacting with PbO, PEG suppresses the formation of the Pb-deficient pyrochlore phase and aids the formation of the perovskite phase. Compared with the two-step columbite method and the complicated sol−gel method to synthesize the perovskite materials, the method introduced in this communication is simple and low cost. This method can be applied to the synthesis of other Pb-containing and Bi-containing ferroelectric materials, especially the relaxors, in which the pyrochlore phase is difficult to eliminate.

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Supporting Information Available: Prepration procedure of PMN-PT powders with the PEG200-modified conventional solid-state reaction and details of materials charaterization, including XRD, TG/DSC curves, SEM patterns, and EDX analysis, as well as SEM and EDX results. This material is available free of charge via the Internet at http://pubs.acs.org.

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