A rutile precursor method to prepare $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ powders

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Lead magnesium niobate-lead titanate $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3-xPbTiO_3$ (PMN-PT) has been widely investigated for its excellent dielectric and piezoelectric properties, which makes it an ideal material for applications in multiplayer ceramic capacitors, piezoelectric transducers and solid-state actuators [1, 2]. In the conventional process for preparing PMN-PT, undesirable pyrochlore phase is often residual and degrades the dielectric and piezoelectric properties. The most important improvement for the preparation process is the columbite precursor method, which has been developed by Swartz and Shrout *et al.* [3, 4]. In that method, the columbite precursors $MgNb_2O_6$ are fabricated first, then form the PMN-PT with the addition of TiO_2 and PbO. That method provides a reproductive way to prepare near-pure perovskite phase PMN-based material, as well as a comparatively low temperature sintering process for densifying PMNT ceramics. The improvement has aroused extensive interest to the PMN-PT system. The functions of Ti^{4+} ions that shift the maximum dielectric constant (T_m) to higher temperature and induce the high piezoelectric performance have been widely accepted [5, 6]. The investigations of constituent Ti including the behavior of TiO_2 in the process of PMN-PT synthesis are supposed to have significance from both theoretical and practical points of view. However, at the step of precursor preparation, the study of TiO_2 addition is poorly reported. Shrout *et al.* have revealed that the columbite $(Mg_{1/3}Nb_{2/3})_{0.93}Ti_{0.07}O_2$ could be fabricated with addition of a small amount of TiO_2 [7]. However, for the PMN-PT with the compositions around the morphotropic phase boundary (MPB), which is characterized by the coexistence of rhombohedral and tetragonal phases [8], the preparation of $(Mg_{1/3}Nb_{2/3})_{(1-x)}Ti_xO_2$ (MNT) remain unreported.

In this letter, single phase rutile structure $(Mg_{1/3}Nb_{2/3})_{0.67}Ti_{0.33}O_2$ (MNT33) was prepared from the starting material Nb_2O_5, MgO, and TiO_2, subsequently formed the perovskite PMN-PT with the addition of PbO. The phase formation and transition mechanism of MNT33 were investigated by thermal analysis and X-ray powder diffraction.

The rutile precursor MNT33 was calcined at 1250 °C for 4 hrs first, then mixed with PbO, milled, dried, and calcined at 750 and 850 °C to form the perovskites. Meanwhile, The columbite precursor method was applied to fabricate 0.67PMN-0.33PT powders for comparison. Excess 2 mol% PbO was added in both processes in order to promote the perovskites. Aiming at attaining the comprehensive understanding of the phase evolution of rutile MNT33, the synthesis temperatures were subdivided to 1000, 1100, 1200, and 1250 °C to calcine MNT33. In addition, the stoichiometric rutile $(Mg_{1/3}Nb_{2/3})_{0.50}Ti_{0.50}O_2$ (MNT50) was prepared at 1250 °C to show the standard rutile structure. The phase formation and stability were measured by a simultaneous thermogravimetric analysis (TG) and differential thermal analysis (DTA). A heating rate of 10 °C/min was used in an open air. At room temperature, X-ray diffractometer (XRD, Cu K_α) was used to characterize the phase structures of MNT and PMN-PT powders. The scanning conditions were: 2θ from 10° to 70°, scan rate 0.02°/1 s.

DTA curves (shown in Fig. 1) exhibit the difference between MNT33 and $MgNb_2O_6$ mixture. For $MgNb_2O_6$ mixture, there is only a broad exothermic peak with the center at 850 °C, which is a typical feature of solid-state oxide reaction. It can be associated with the formation of columbite $MgNb_2O_6$. However, for the MNT33 mixture, besides a broad exothermic peak, there is another comparatively sharp endothermic peak at about 980 °C.

The XRD patterns of precursor powders calcined at different temperatures (see Fig. 2) exhibit that at the temperature of 1000 °C, the precursor MNT is characterized by the coexistence of columbite $MgNb_2O_6$ and rutile MNT33, and the columbite is dominant over the rutile phase. It implies that the beginning of the formation of rutile MNT33 is around 1000 °C. As the temperature elevates to 1100 and 1200 °C, the diffraction intensity of rutile increasingly enhances and that of columbite decreases, which indicates the transition from columbite $MgNb_2O_6$ to rutile MNT33. At the temperature 1250 °C, the precursors are single-phase rutile MNT33, which matches the stoichiometric rutile MNT50 (JCPDS 40–0336). These data are critical to explicate the DTA curve for MNT33. The broad peak with the center at 820 °C, in the same manner, can be attributed to the formation of $MgNb_2O_6$, and the comparatively sharp endothermic peak around 980 °C should result from the formation of rutile MNT33, which evolves from the reaction between $MgNb_2O_6$ and TiO_2. The reaction formula

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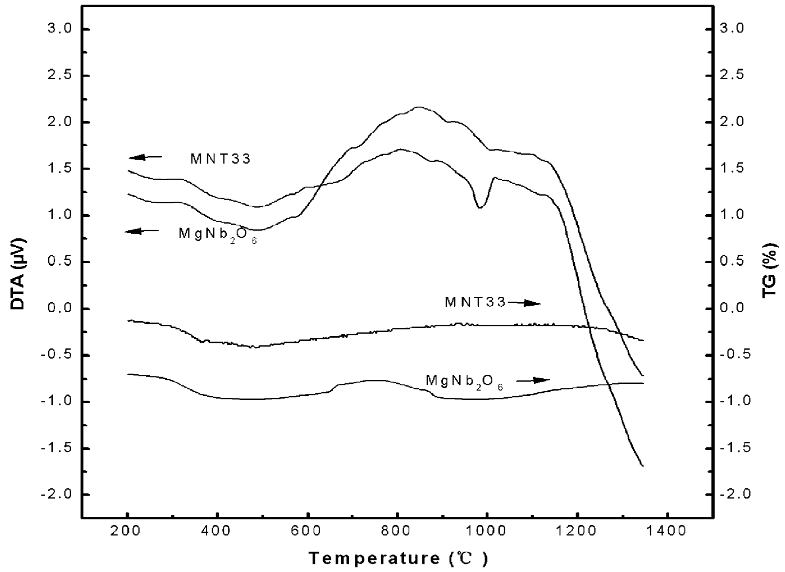

Figure 1 TG-DTA curves for MNT33 and $MgNb_2O_6$ mixture.

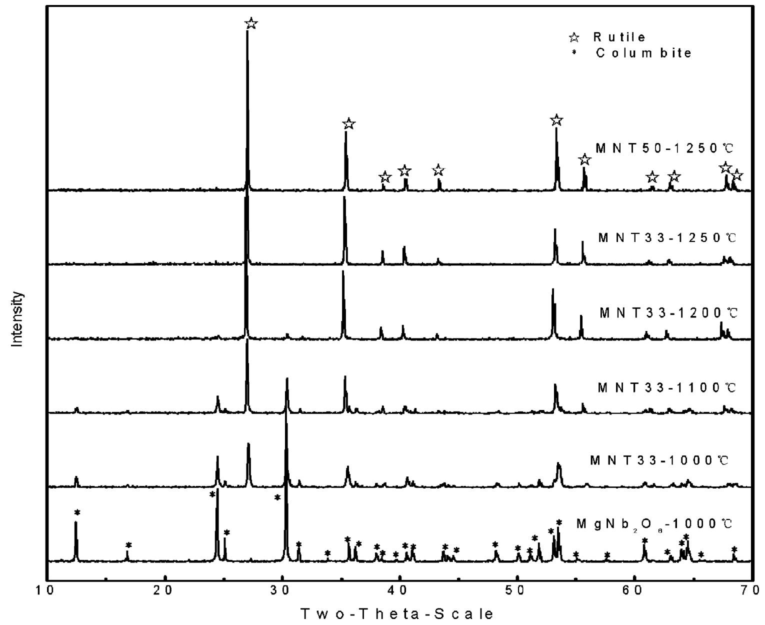

Figure 2 XRD patterns for $MgNb_2O_6$ and MNT33 calcined at different temperatures.

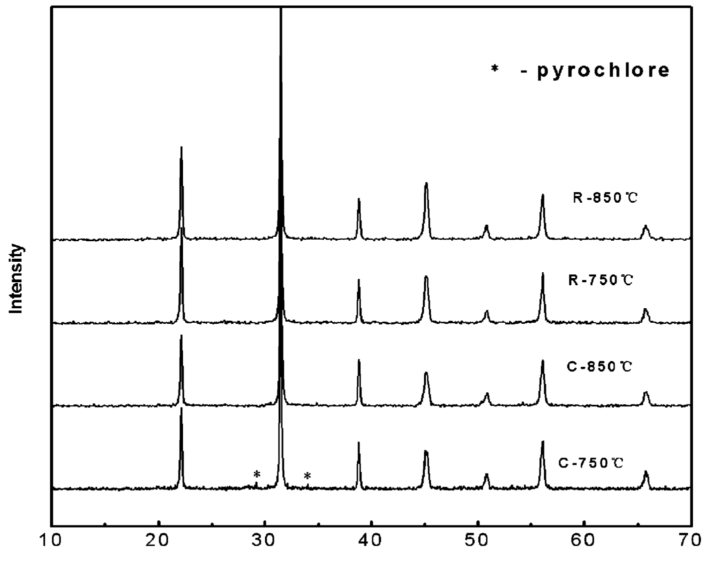

Figure 3 XRD patterns for 0.67PMN-0.33PT prepared by different processes; R stands for the rutile precursor method, and C stands for the columbite precursor method.

should be:

$$0.67\ \mathrm{MgNb_2O_6} + 0.99\mathrm{TiO_2} \rightarrow 3(\mathrm{Mg_{1/3}Nb_{2/3}})_{0.67}\mathrm{Ti_{0.33}O_2}.$$

At the temperature of 1250 °C, the reaction is complete and single phase rutile forms. The TG curves for mixture of MNT33 and $MgNb_2O_6$ demonstrate that there is no significant weight loss up to 1350 °C during the process of solid-state reaction.

The XRD patterns of the 0.67PMN–0.33PT powders prepared by different processes are shown in Fig. 3. It indicates that the pure perovskite PMN-PT powders can be obtained at the temperature of 750 °C by the rutile precursor method. However, for the columbite precursor method, a small amount of pyrochlore exists as the PMN-PT was calcined at 750 °C. In the present columbite process, only if the temperature elevates to 850 °C, the pyrochlore is below the detection limit. The rutile precursor method with the advantage to suppress pyrochlore over the columbite precursor method at low temperature may be due to the factor that the structure of rutile (tetragonal) is closer to perovskite than that of columbite (orthorhombic), and consequently it is easier to form the pyrochlore-free perovsktes.

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