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Perovskite phase formation in the $PbMg_{1/3}Nb_{2/3}O_3$–$PbZrO_3$–$PbTiO_3$ system by the columbite route

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The reaction mechanism of $PbMg_{1/3}Nb_{2/3}O_3$–$PbZrO_3$–$PbTiO_3$ (PMN–PZT) perovskite phase prepared by the columbite route has been studied in the temperature range from 600 to 800 °C. The effects of heating and cooling rate during the calcination of 3PbO + $MgNb_2O_6$ + PZT powder mixtures have also been investigated. Nearly pure perovskite phase, 0.9 PMN–0.1 PZTsolid solution with no pyrochlore phase, as determined by X-ray diffraction, could be prepared at 800 °C for 2 h. From DTA/TGA, dilatometry and XRD data the reaction mechanism of PMN–PZT solid solution formation could be divided into three steps: (i) decomposition of columbite ($MgNb_2O_6$) by reacting with PbO at 350 to 600 °C (ii) the formation of a B-site-deficient pyrochlore phase $Pb_2Nb_{1.33}Mg_{0.17}O_{5.50}$ at close to 650 °C, and (iii) the formation of perovskite phase PMN–PZT solid solution from the reaction of $Pb_2Nb_{1.33}Mg_{0.17}O_{5.50}$ pyrochlore phase with MgO and PZT above 650 °C.

1. Introduction

Considerable effort to clarify the reactions occurring in the formation of $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) has been expended by a number of researchers [1–7]. In a general manner the results reported by the major contributors agree that the cubic pyrochlore phase $Pb_3Nb_4O_{13}$ (P_3N_2) is the first product to be formed, between 500 and 600 °C, when the mixed oxide technique was used [1–5]. A second stage takes place between 600 and 700 °C in which the $Pb_3Nb_4O_{13}$ reacts with PbO to give a rhombohedral pyrochlore, $Pb_2Nb_2O_7$ (P_2N) according to the results of Inada [1], a Pb-rich cubic pyrochlore phase $Pb_3Nb_2O_8$ (P_3N) in the sequence reported by Lejeune and Boilot [2] or a rhombohedral pyrochlore phase with formula $Pb_5Nb_4O_{15}$ (P_5N_2) as reported by Bouquin *et al.* [3]. Above 700 °C the different reported pyrochlore phases reacted with MgO to give the PMN cubic perovskite phase. Dambekalne and co-workers [5, 6] reported a different reaction sequence in the binary PbO–Nb_2O_5 system. The low-temperature cubic pyrochlore phase P_3N_2 was not detected but only the rhombohedral pyrochlore P_2N one.

According to the results reported by Swartz and Shrout [4], when an intermediate step like the prereacting of MgO and Nb_2O_5 to give $MgNb_2O_6$ (columbite) is used, the subsequent reaction with PbO leads to almost pyrochlore-free ($\leq 5\%$) PMN phase, and Guha and Anderson [7] also reported the preparation of pure PMN by starting from an intermediate compound like the cubic pyrochlore $Pb_3Nb_2O_8$. On the other hand, if a sol–gel route is chosen for PMN synthesis, as reported by Chaput *et al.* [8], progressive MgO insertion into a B-site-deficient cubic pyrochlore led to the formation of PMN perovskite phase just above 700 °C.

It seems obvious that the cubic perovskite PMN phase can be synthesized by the solid-state reaction $3PbO + MgO + Nb_2O_5 \rightarrow Pb(Mg_{1/3}Nb_{2/3})O_3$, and that such a reaction cannot proceed in only one step. In a powder mixture of the reactant oxides three types of intergranular contact point exist and, at these, those intermediate products having the lowest formation enthalpy will be formed first and then further react to form PMN as the final reaction product. At the end of this reaction process an unwanted pyrochlore phase, very difficult to eliminate, persists along with the perovskite phase. Rigorous control of the different processing parameters influencing the reaction kinetics will help to minimize or even avoid the formation of the undesirable pyrochlore phase.

It is well known that the presence of that pyrochlore phase, even in small quantities, has a negative effect on the dielectric properties of PMN ceramics [9]. As lead magnesium niobate is a very promising candidate for use as multilayer capacitors, its reliability will be conditioned by those parameters which detrimentally affect the properties such as dielectric constant, dielectric losses and volumetric efficiency. Therefore, once a well synthesized PMN powder is achieved it becomes necessary to control other processing parameters in order to obtain adequate and reproducible sintering–microstructure–properties relationships.

The goals of the present work were (a) to investigate the subsolidus compatibility between various phases in the quinary system PbO–MgO–Nb_2O_5–

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TiO_2–ZrO_2, and (b) to study the reaction kinetics of PMN formation in a composition 0.9PMN–0.1PZT containing an excess of PbO by using the columbite route.

2. Experimental procedure

In all cases the materials were prepared from powders of a mixture of lead oxide ($\geq$ 99.8 pure from Merck, Germany), a high specific surface ($\geq 13\ m^2\,g^{-1}$) prereacted lead zirconate titanate (PZT), and a presynthesized columbite, $MgNb_2O_6$ (MN). The PMN–PZT powder mixture preparation consists of two stages: in the first one $MgNb_2O_6$ was prepared by reaction of Nb_2O_5 powder (Fluka Buchs, Switzerland) with MgO powder (Fisher Scientific, Pittsburg) (both of them 99.99% pure) at 1000 °C for 4 h, attrition milling for 2 h and drying. At end of this preparation process the specific surface of the synthesized $MgNb_2O_6$ powder was $2.8\ m^2\,g^{-1}$. In the second stage a mixture of PbO and prereacted PZT was added to the columbite powder, attrition-milled for 2 h in ethanol and slowly dried in an oven. The PMN–PZT composition contained 10 mol% PZT and, in this last, the PZ/PT ratio was 40/60. Also an excess of 4.1 wt % PbO was added.

One part of the powder mixture containing the appropriate amounts of PbO, PZT and $MgNb_2O_6$ was taken to study PMN–PZT solid-solution reaction formation by the following schedule. (a) The powders were first placed in a small platinum crucible and subjected to the reaction temperature in a preheated furnace. The heat treatments were carried out in air at a fixed temperature between 600 and 800 °C. After subjecting the samples to the different reaction temperatures they were air-quenched and ground. Finally (b) the small platinum crucibles containing the powders were placed in a furnace and heated at a controlled rate of $240\ °C\,h^{-1}$, followed by cooling in the furnace.

The phase composition of the reaction products was determined by X-ray diffraction analysis (XRD) (Siemens D-5000 diffractometer, CuK_α radiation, 40 kV, 50 mA). Although Nb_2O_5–MgO–PbO–TiO_2–ZrO_2 is a very complex system, the different phases formed during PMN formation are characterized by good symmetry and, therefore, the intensity of the diffraction lines could be used to estimate the progress of the reaction. In this way, the equation $X_i = KI_i/I_{0i}$ was used to calculate the approximate concentration of the different phases (X_i = phase concentration, I_i = intensity of the diffraction line for the phase i in the reaction product, I_{0i} = intensity for the same diffraction line in the pure phase, K = constant). The diffraction lines (1 1 1), (1 1 3), (2 2 2) and (1 1 0) were used for PbO, $MgNb_2O_6$ (columbite), P_yMN (pyrochlore phase) and PMN (perovskite phase), respectively. In order to know which is the first reaction product to be formed during PMN formation, two complementary techniques were utilized: differential thermal and thermogravimetric analysis (DTA/TGA) (Mettler model TA-200) with Al_2O_3 as a reference material, in air from 20 to 800 °C and a heating rate of $8\ °C\,min^{-1}$, and dilatometry (Adamel Lhomargy DI-24 dilatometer, Paris) with a heating rate of $5\ °C\,min^{-1}$.

On the other hand, to know the subsolidus phase compatibility in the quinary Nb_2O_5–MgO–PbO–TiO_2–ZrO_2 system several compositions, containing the end-members of the corresponding tie-lines, were heat-treated up to 800 °C for several hours. At the end of the run the samples were air-quenched and the phases present were identified by XRD. These solid-phase compatibility experiments were carried out on the possible pseudobinary sections PMN–Z, PMN–PZ, MN–PZ, MN–T, PMN–T, MN–PT and M_4N–PT.

3. Experimental results

3.1. Subsolidus phase relations

The subsolidus phase compatibility study was carried out on compositions previously calcined at 800 °C for 3 h, then milled, re-pressed and heated again at 800 °C for 12 h. Under these experimental conditions neither appreciable PbO volatilization (< 0.3%) nor melt formation took place, and thus a preliminary subsolidus phase compatibility diagram, as shown in Fig. 1 for the system PbO–MgO–Nb_2O_5–TiO_2–ZrO_2, could be established.

According to our results two ternary compounds exist, perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) and cubic pyrochlore $Pb_2Nb_{1.33}Mg_{0.17}O_{5.50}$ (P_yMN). In close agreement with the previously reported results of Guha and Anderson [10], the perovskite is compatible with both PbO and MgO and also with TiO_2 and ZrO_2. However, it is not compatible with Nb_2O_5.

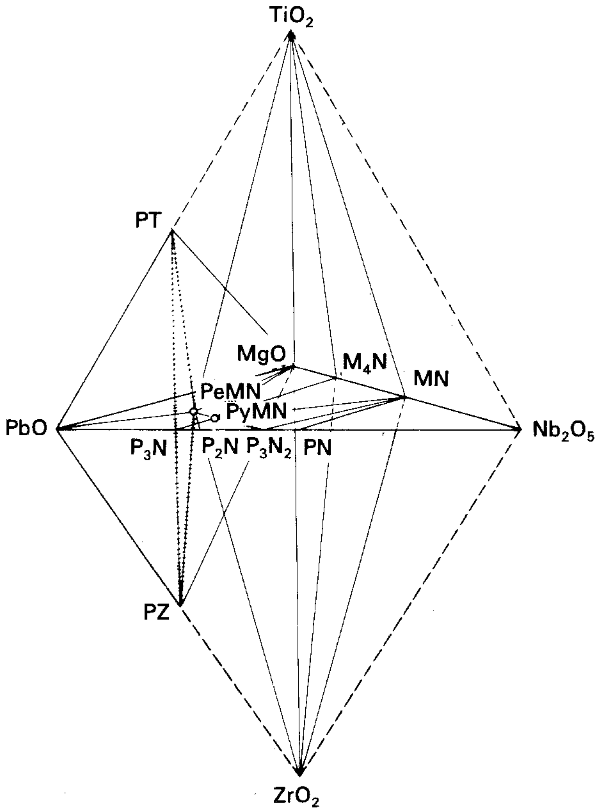


Figure 1 Subsolidus phase compatibility in the quinary system PbO–MgO–Nb_2O_5–ZrO_2–TiO_2 at 800 °C.

Some results contradicting those reported by Guha and Anderson [10] were found. For example, $PbTiO_3$ is not compatible with either $MgNb_2O_6$ or $Mg_4Nb_2O_9$, and the reaction between these phases leads to the formation of ternary pyrochlore P_yMN and TiO_2. In the same way $PbZrO_3$ is not compatible with the two above niobates. The hatched lines in Fig. 1 indicate complete solid solutions between the end-member phases PMN–PZ, PZ–PT and PMN–PT. The subsolidus phase relationships shown in Fig. 1 also incorporate the results of Guha and Anderson [10] on the quaternary system PbO–MgO–Nb_2O_5–TiO_2.

3.2. PMN–PZT solid solution formation

3.2.1. *Differential thermal analysis*

Fig. 2 shows the DTA/TGA curves obtained for the PbO, $MgNb_2O_6$ and PZT powder mixture. An endothermic peak at 110 °C attributed to the loss of residual humidity water was present, and an exothermic effect at about 160 °C due to the combustion of some residual organic solvent was also detected. A small endothermic peak at 280 °C could be due to the removal of some residual hydroxyl groups in the powder mixture. Between 340 and 600 °C a wide endothermic process was shown which is attributed to the reaction of PbO with the columbite $MgNb_2O_6$. At about 600 °C such an endothermic reaction was complete and a clear pyrochlore phase formation, evidenced by the exothermic peak between 600 and 700 °C, emerged. Above 700 °C an endothermic reaction process attributed to the perovskite PMN formation took place which, apparently, finished at about 850 °C.

3.2.2. *Dilatometry*

Fig. 3 shows the dilatometric curve obtained on a compacted 3PbO–$MgNb_2O_6$–PZT powder mixture in the temperature range 20 to 800 °C. A strong expansion between 400 and 620 °C followed by an intense thermal shrinkage at 630 to 750 °C mainly characterized the dilatometric behaviour. Above 750 °C a new expansion step seems to be present.

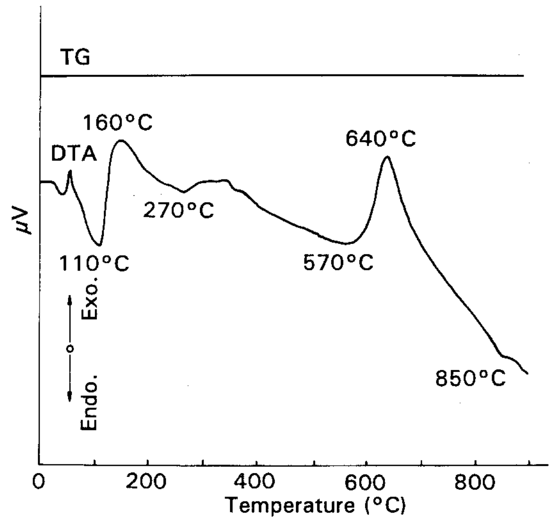


Figure 2 DTA/TGA curves at constant heating rate of 8 °C min^{-1} for the 3PbO–$MgNb_2O_6$–PZT powder mixture.

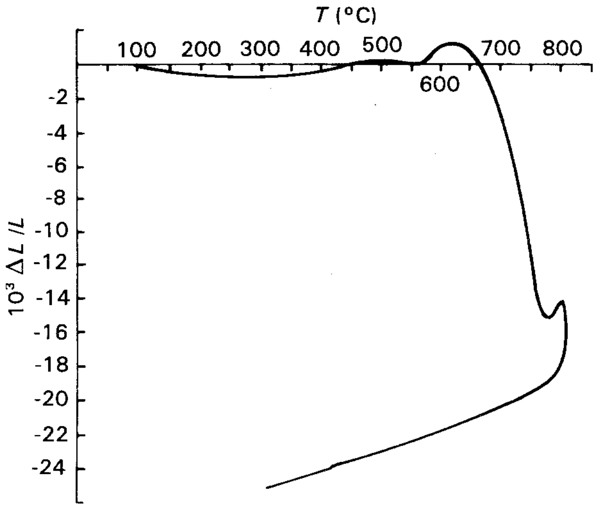


Figure 3 Dilatometric expansion characteristics of the 3PbO–$MgNb_2O_6$–PZT powder mixture at constant heating rate of 5 °C min^{-1}.

3.2.3. *X-ray diffraction*

As mentioned in section 2, quantitative analysis of the phases during PMN–PZT solid solution formation can be difficult. However, as shown below an estimation of the phase composition in the reacting mixture as a function of temperature was made as follows.

3.2.3.1. From air-quenched powder mixture. A set of preliminary experiments with a powder mixture of composition 0.9PMN–0.1PZT (PZ/PT = 40/60) showed that after heating at 600 °C for 4 h the products contained PbO, MN and PZT, which indicates that below that temperature no reaction took place. As the temperature was increased a very important feature was observed between 600 and 700 °C. In that narrow temperature range the reaction mainly proceeds, in a first step, at intergranular PbO–MN contacts according to the following equation:

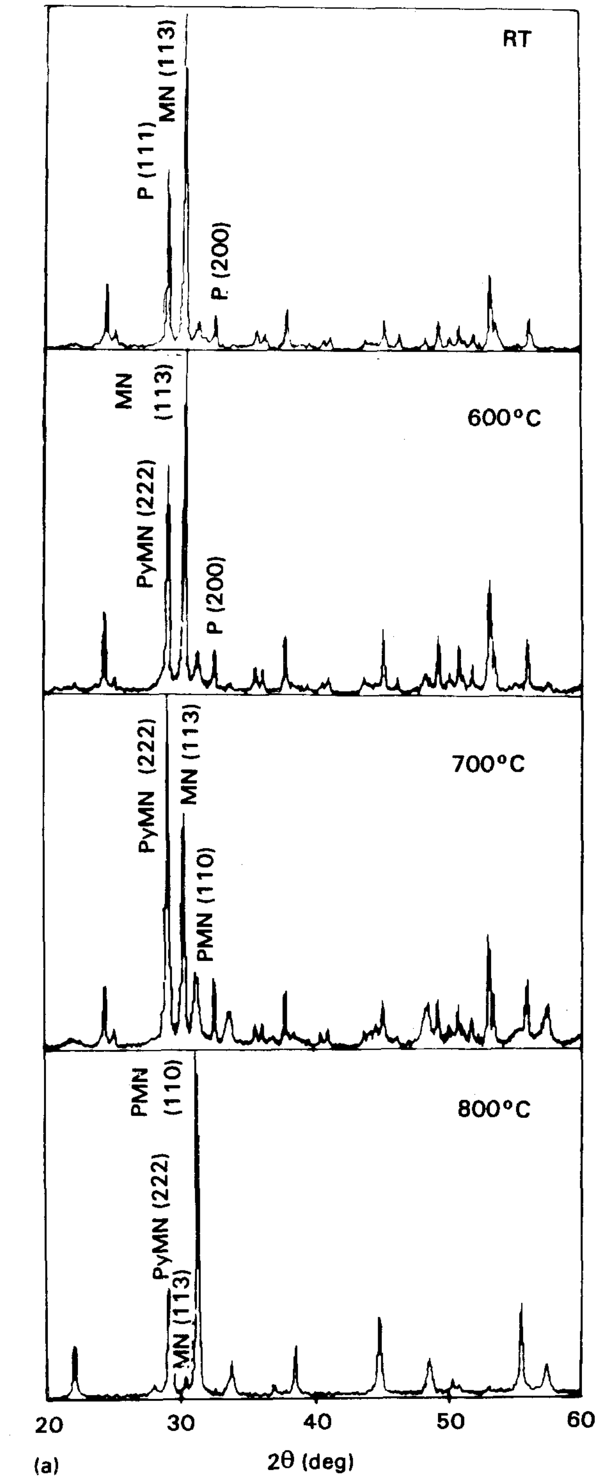
$$3PbO + MN \rightarrow \text{pyrochlore phase} + MgO \xrightarrow{>600^\circ} P_yMN$$

in which the oxygen octahedral structure of the columbite ($MgNb_2O_6$) is broken with the formation of a growing (P_3N or P_3N_2) disordered pyrochlore phase and very active free MgO. It seems that this MgO was rapidly incorporated, with rising temperature, into the pyrochlore structure. If this is so then the pyrochlore phase formed could be P_3N which, having a partially vacant BO_6 octahedral sublattice, would easily accommodate the MgO. In this process the P_3N pyrochlore phase is continuously nucleated and simultaneously reacted with MgO to give rise to P_yMN formation. The lattice parameter of the pyrochlore phase shifted from $a = 1.072 \pm 0.005$ nm at room temperature to $a = 1.060 \pm 0.005$ nm at 800 °C. If it is assumed that the PMN perovskite phase is formed by the insertion of Mg^{2+} ions into the P_3N or $Pb_2Nb_{1.33}O_{5.33}$ B-deficient pyrochlore structure, then the above lattice parameter corresponds to an insertion of about 25 wt %, which leads to a formula $Pb_2(Nb_{1.33}Mg_{0.17})O_{5.50}$.

The above reaction takes place up to approximately 700 °C, and more than 60–70% of the P_yMN pyrochlore phase was formed as estimated from the intensity of the diffraction lines (Fig. 4a). Just below 700 °C and before the P_yMN pyrochlore phase formation was completed a new phase, the cubic perovskite PMN solid solution, starts to appear. This last reaction simultaneously proceeds above 650 °C, in a second step, by diffusion of some of the PbO, MgO and PZT into the lattice of the P_yMN pyrochlore phase, leading to the formation of the PMN–PZT solid solution according to the equation

$$P_yMN + MgO + PbO \xrightarrow[> 650°]{+\ PZT} (PMN\text{–}PZT)_{ss}$$

Above 700 °C, and in the narrow temperature range of 700 to 800 °C, the perovskite PMN phase formation was almost complete. This assumption was supported by the fact that the intensities of the diffraction lines corresponding to PbO, residual MN and P_yMN strongly decrease while those corresponding to the perovskite PMN solid solution increased (Fig. 4b). It seems probable that the diffusion of Mg^{2+} ions in the P_yMN pyrochlore surface leads to a saturated magnesium pyrochlore phase layer which acts as a support for PMN–PZT solid solution formation. It must be noted that perovskite PMN phase completion was not achieved below 800 °C, and a residual amount (8–10%) of the pyrochlore phase remained even above that temperature. It seems also probable that the diffusion rate of Mg^{2+} ions into the lattice of the saturated magnesium pyrochlore phase could be rate-limiting in the formation of PMN–PZT solid solution. Apparently the additive PZT plays its role only when the temperature is higher than 700 °C.



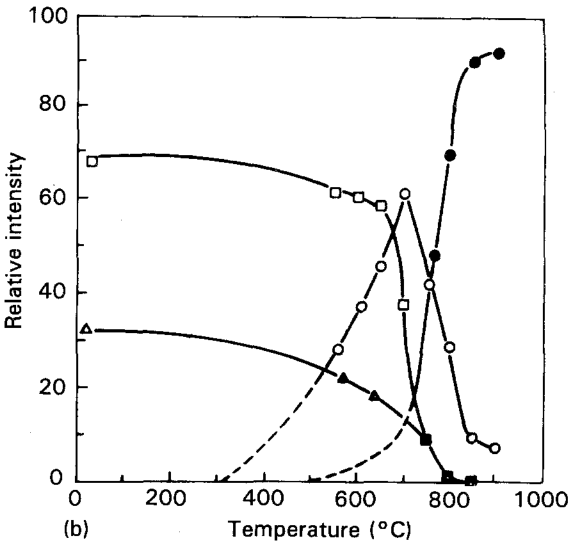
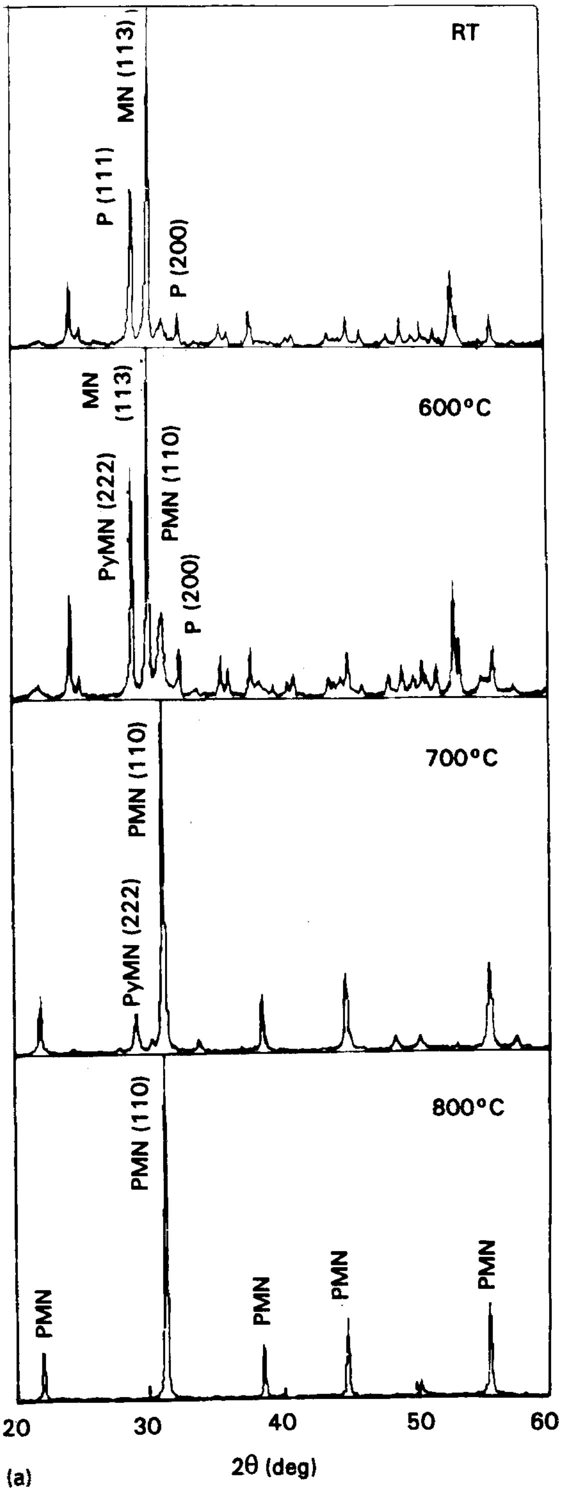


Figure 4 XRD results for (a) air-quenched $3PbO–MgNb_2O_6$–PZT powder mixtures from the indicated temperatures, and (b) phase composition of the reacting mixtures as a function of temperature: (△) P, (□) MN, (●) PMN, (○) P_y MN.

3.2.3.2. From controlled heating-rate powder mixture. As can be seen from Fig. 5a and b, cubic perovskite phase was always the main reaction product to be formed from 600 °C. PMN–PZT solid solution formation was complete at 800 °C for a 2 h cycle and no other reaction products were clearly detected. However, according to the DTA results (Fig. 2) an exothermic process takes place between 600 and 700 °C which could be associated with pyrochlore phase formation. It seems that its formation runs parallel with the simultaneous interaction of MgO and PZT to give PMN, and that the latter took place at a higher rate than that of pyrochlore phase formation. On the other hand, it was also found that the reaction rate for PMN–PZT solid solution formation was higher than when an air-quenched powder mixture was used.

4. Discussion

The experimental results show the strong influence of the heating and cooling rates on the reaction products formed during the calcination of powder mixtures leading to the formation of PMN–PZT solid solution. The following mechanism for perovskite phase formation in the temperature range from 600 to 800 °C, when columbite ($MgNb_2O_6$) was used as the starting raw material, could be advanced. In reaction sequence (a) (Section 2) PbO reacts at 600 °C, in a first step, with $MgNb_2O_6$ to give a B-deficient P_3N pyrochlore phase which, having a partially vacant BO_6 octahedral sublattice, simultaneously incorporates some of the free MgO produced in that reaction leading to the formation of a pyrochlore phase with an unknown nominal composition. However, the lattice parameter measured for this phase was $a = 1.060 \pm 0.005$ nm, from which the amount of MgO inserted could be assumed to be approximately 25 wt % and, therefore, the formula for the pyrochlore phase will be $Pb_2Nb_{1.33}Mg_{0.17}O_{5.50}$ (P_yMN). Such a composition contrasts with both a similar B-deficient pyrochlore phase recently proposed by Chaput *et al.* [8] ($Pb_2Nb_{1.33}Mg_xO_{5.33+x}$ with $0 < x < 0.66$, for which a lattice parameter of $a = 1.062$ nm was reported) and an A-deficient pyrochlore phase such as $Pb_{1.83}(Nb_{1.71}Mg_{0.29})O_{6.39}$ with a lattice parameter of $a = 1.059$ reported by Shrout and Swartz [11]. From those results it could be assumed that the difference in both the lattice parameters measured and the suggested structures could be related to the amount of MgO incorporated as a function of temperature. When the P_yMN pyrochlore phase formation was almost complete, as determined by X-ray diffraction (see Fig. 4), some of MgO reacts further to give an MgO-saturated P_yMN pyrochlore phase.



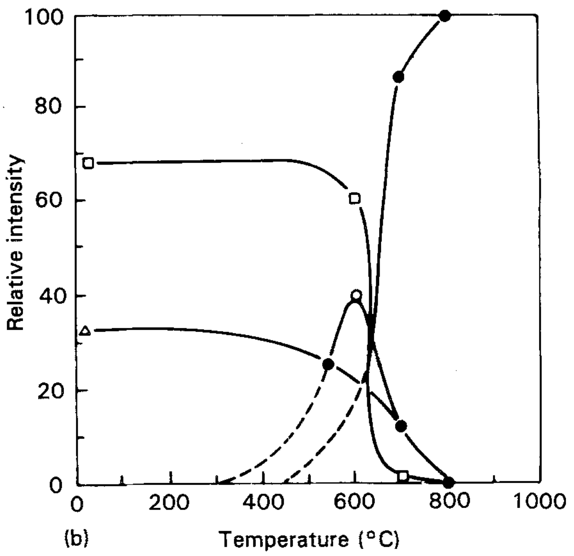


Figure 5 XRD results of (a) controlled heating-rate $3PbO–MgNb_2O_6$–PZT powder mixtures at the indicated temperatures, and (b) phase composition of the reacting mixtures as a function of temperature: (△) P, (□) MN, (●) PMN, (○) P_y MN.

If the temperature was increased above 650 °C, then the interaction of P_yMN with more MgO and PZT takes place in a second reaction step, forming the PMN–PZT solid solution as the final reaction product. According to our results it is clear that the dominant phase to form perovskite is the P_yMN pyrochlore phase that acts as a host matrix in which the interdiffusion of Mg^{2+}, Ti^{4+} and Zr^{4+} ions led to PMN–PZT solid solution formation. The perovskite phase was not completely formed even above 800 °C, with 6–8% of the P_yMN pyrochlore phase remaining.

In reaction sequence (b) both the pyrochlore P_yMN and the perovskite PMN phases seem to be the two

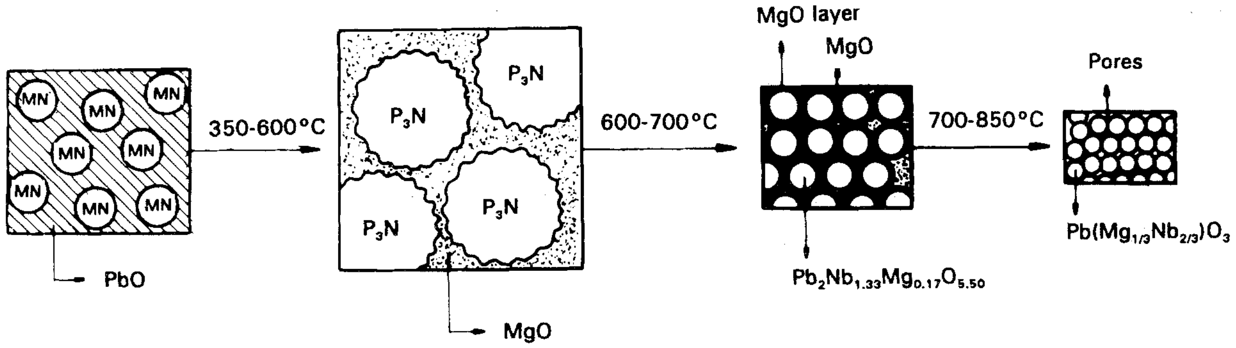


Figure 6 Schematic diagram of perovskite phase formation.

main reaction products up to 600 °C. In the narrow temperature range of 600 to 700 °C the perovskite PMN phase formation was almost complete, coexisting with less than 4% of P_yMN pyrochlore phase (see Fig. 5). At 800 °C the PMN–PZT solid solution with perovskite structure was the only phase present.

Combining the above XRD results, obtained in the temperature range of 600 to 800 °C, with those of DTA/TGA and dilatometric curves it could be assumed that, as schematically shown in Fig. 6, the overall reaction mechanism of perovskite phase formation is dominated by the formation of a pyrochlore phase which is the required nucleous for the perovskite PMN–PZT phase formation. Such a pyrochlore phase, assumed to be $P_3N(Pb_2Nb_{1.33}O_{5.33})$, was nucleated during the $MgNb_2O_6$ decomposition by reaction with PbO, as shown in Fig. 2 by the endothermic reaction process between 350 and about 600 °C, and corroborated by an expansion in the dilatometric curve. When such an endothermic reaction, not previously reported in the literature, goes to completion then an exothermic reaction process takes place which, starting at 600 °C, had its maximum development at 650 °C in close agreement with XRD data (see Fig. 4b) and connected with the strong shrinkage of the sample in the same temperature range in the dilatometric studies (see Fig. 3). A similar exothermic effect was found by Bouquin *et al.* [3] in studying PMN–PT solid solution formation, but no explanation for such a phenomenon was given. In the same way Chaput *et al.* [8] observed only the formation of a cubic pyrochlore phase but the authors did not show any DTA experimental evidence to corroborate their findings. They proposed that the pyrochlore phase directly transformed into the perovskite phase by insertion of Mg^{2+} ions.

5. Conclusions

Reaction mechanisms of $Pb(Mg_{1/3}Nb_{2/3})O_3$ prepared by the columbite route have been investigated in the temperature range from 600 to 800 °C, and it was found that the formation mechanism of the PMN–PZT perovskite vary with the heating and cooling rates used during the calcination of 3PbO + $MgNb_2O_6$ + PZT powder mixtures. A pure perovskite phase, 0.9PMN–0.1PZT with no pyrochlore phase (as determined by X-ray diffraction), could be prepared at 800 °C for 2 h. Depending on the heating and cooling rates used in calcining the above powder mixtures, the formation mechanism of the PMN–PZT perovskite could be dominated or not by a P_3N pyrochlore phase. Combining the DTA, dilatometry and XRD data the reaction mechanism of $Pb(Mg_{1/3}Nb_{2/3})$–$Pb(Zr_{2/5}Ti_{3/5})O_3$ formation could be divided into three steps, namely (i) the decomposition of $MgNb_2O_6$ by reaction with PbO between 350 and 600 °C, (ii) the formation of $Pb_2Nb_{1.33}Mg_{0.17}O_{5.50}$ pyrochlore phase at close to 650 °C, and (iii) formation of PMN–PZT solid solution from the reaction of $Pb_2Nb_{1.33}Mg_{0.17}O_{5.50}$ with MgO and PZT above 650 °C.

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