Evidence of the Tetragonal and Rhombohedral Phases Co-Existence in the 0.9Pb(Zr_{0.52}Ti_{0.48})O_3 – 0.1Pb(Mg_{1/3}Nb_{2/3})O_3 Ceramics

Rungnapa Tipakontitikul and Anuson Niyompan

Department of Physics, Faculty of Science, Ubon Rajathani University, Ubon Ratchathani, 34190, Thailand.
Phone: +66 45 288381, Fax: +66 45 288381, E-Mail: rungnapa@rocketmail.com

Abstract

The 0.9PZT-0.1PMN ceramics was prepared employing a mixed oxides method. The XRD results reveal co-existence between tetragonal ad rhombohedral phases. Quantitative analysis according to the Rietveld method provides relative concentration of these two phases and these seem to be sensitive to sintering temperature. Sintering temperature induce a higher relative concentration of the tetragonal with also a higher densification. Presence of the tetragonal phase also effect the dielectric constant in a direction of positive proportion.

1. Introduction

The ternary phase diagram of the lead zirconate titanate (PZT) - lead magnesium niobate (PMN) solid solution was determined by Ouchi et al. [1] in early forties. Substitution of magnesium (Mg^{2+}) and niobium (Nb^{5+}) (approximately 20 mol%) in PZT changed the phase stability from tetragonal to rhombohedral, near the structural morphotropic phase boundary (MPB) [1,2]. Later, the structure and dielectric responses indicated the presence of tetragonal and pseudo-cubic phases in the composition 0.875PZT-0.125PMN which has the highest values of the dielectric constant [3]. However, the dielectric and electromechanical properties has been decreases due to an increased pseudo-cubic non-ferroelectric phase content. Further increase in the dielectric properties results in another change in phase stability from ferroelectric rhombohedral to ferroelectric tetragonal.

The boundary between the ferroelectric tetragonal and rhombohedral phases is nearly dependent of sintering temperature and is known as an MPB [4]. Compositions close to this boundary are known to exhibit some of the highest piezoelectric coupling coefficients, as well as maximum dielectric constant. The mechanism resulting in enhanced properties is believed to be due to the coexistence of tetragonal and rhombohedral phases in the MPB. Boutarfaia et al. [5] confirmed the coexistence of these phases and explained the behavior in terms of compositional fluctuations in the PZT. Lead magnesium niobate is one of the extensively investigated relaxor materials because of its high dielectric constant response and suitable for technological applications. This materials easily forms a solid solution with lead titanate, enhances the dielectric properties, and shifts the dielectric maximum to the higher-temperature side. However, no evidence of a rhombohedral-tetragonal phase transformation near a MPB has been reported for these binary systems. The aim of the present work was to study the phase transformation in a crystalline solution of PZT and PMN using X-ray diffraction (XRD) which also put on the analysis of the XRD data, because this may give a clue to understand the dielectric response in this system.

2. Experimental

The powders of 0.9PZT-0.1PMN were synthesized by the conventional route, using a two-stage synthesis process. The columbite structure (MgNb_2O_6 or MN) and wolframite structure (ZrTiO_4 or ZT) were synthesized and described in Ref. 6-7. The calcined MN and ZT powders were mixed with PbO in a stoichiometric ratio form the 0.9PZT-0.1PMN. After gridding and sieving, the calcined powder was mixed with 3 wt% polyvinyl alcohol binder and then pressed into a pellet. Binder burnout occurred by slowly heating to 500 °C. Sintering process were carried out between the temperature range
1200-1275 °C with a constant dwell time of 4 h and fixed heating/cooling rate of 10 °C/min. To prevent lead loss during sintering, the pellets were sintered in a close alumina crucible containing PbZrO₃ powder.

The densities of the sintered samples were determined using Archimedes’s method. The crystal structure and lattice parameters were determined from XRD patterns that were recorded with CuKα radiation at room temperature over the angular range of $20^\circ \leq \theta \leq 60^\circ$ by step of 0.01°. The qualitative analysis has been carried out using the Rietveld method.

The dielectric permittivity was calculated from impedance data (Hp model 4284A) obtained at 1 kHz in a temperature range from room temperature to 400 °C.

3. Results and discussion

![Fig.1 XRD patterns of 0.9PZT-0.1PMN ceramics sintered at various temperatures.](image)

The XRD patterns of samples sintered at temperature ranging from 1200 °C to 1275 °C, revealed the coexistence of tetragonal and rhombohedral phases, which are characterized by reflections splitting in triplets of type (002)T, (200)R and (200)T (Fig.1). This may associate to variations of composition which may lead to a diffuse MPB between the tetragonal and rhombohedral phase.

Extension of the peaks at $\theta \sim 42-47^\circ$ (Fig. 2) shows broader peaks with increasing sintering temperature. Variation of these diffraction lines as a function of sintering temperatures could be explained by the compositional fluctuations which lead to the formation of very small regions rich in tetragonal grains of ceramics.

![Fig. 2 Comparison of (002)T, (200)R and (200)T reflections for 0.9PZT-0.1PMN ceramics.](image)

Table 1 shows the effect of sintering temperature on the sintered density of samples. It is found that the density increased with sintering temperature. The optimum firing temperature for the maximum density, $\rho$, of the ceramic is found to be between 1200 and 1275 °C. The maximum density for sample obtained at 1275 °C is about 95.2% of the theoretical value (TD). The optimum sintering temperature was taken as the point when the PbO vapour pressure evaporation-recondensation equilibrium was established.

<table>
<thead>
<tr>
<th>Sintering temp. (°C)</th>
<th>% TD (g/cm³)</th>
<th>Qualitative concentrations of phases (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1200</td>
<td>92.52</td>
<td>Tetragonal 36.99, Rhombohedral 63.01</td>
</tr>
<tr>
<td>1225</td>
<td>92.25</td>
<td>Tetragonal 34.28, Rhombohedral 65.72</td>
</tr>
<tr>
<td>1250</td>
<td>93.74</td>
<td>Tetragonal 77.04, Rhombohedral 22.96</td>
</tr>
<tr>
<td>1275</td>
<td>94.29</td>
<td>Tetragonal 69.66, Rhombohedral 30.34</td>
</tr>
</tbody>
</table>
The temperature dependence of the dielectric constant and tan δ at 1 kHz of 0.9PZT-0.1PMN ceramics are demonstrated in Fig.3. The samples show the characteristics of a normal ferroelectric material (PZT) with the maximum dielectric constant of nearly 30000 at 1 kHz. This value is much higher than the reported values for pure PMN and PZT ceramics. For tan δ results, it can be seen that low level is observed in the range from room temperature to about 200 °C.

Fig. 3 Temperature dependence of dielectric constant and tan δ of 0.9PZT-0.1PMN ceramics with various sintering temperature.

The results also show that the dielectric constant is increased with increasing sintering temperature and this corresponding to increasing of relative concentration of the tetragonal phases. Actually, presence of tetragonal phase always gives a lower dielectric constant value comparing to that of rhombohedral phase. Thus, in this particular system, the tetragonal phase should affect to the dielectric respond of the rhombohedral phase and give a somewhat over all lower dielectric constant. So far, there is no an appropriate explanation for these results. The possible mechanism may from the effect of tetragonal phase on the spontaneous polarization of the rhombohedral phase. Such effect may fluctuate the polarization orientation of the rhombohedral as they are of 8 possible orientations in [111] while they are only six possible orientations in [100] for tetragonal [8].

4. Conclusions
The solid solution of PZT-PMN ceramics were prepared via the conventional method. Phase identification show coexistence of tetragonal and rhombohedral phases evidenced by peaks at 20 – 42.47°. While the dielectric measurement have shown the dependency of dielectric constant on the relative concentration of the tetragonal phase, one which also found to increase with sintering temperature.

Acknowledgements
The authors acknowledge the Faculty of Science, Ubon Ratjatanee University, Thailand for the equipment support.

References