Study of potassium additive on the phase formation and ferroelectric properties of 0.9PMN–0.1PT ceramics

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Abstract

A recent and innovative method to include Ti into the columbite precursor has permitted to synthesize 0.9PMN–0.1PT powders with high homogeneity. The present work describes this methodology, named modified columbite method, showing that the reaction between MNT and PbO at 800 °C for 2 h results in perovskite single-phase. The crystal structure alterations in the columbite and perovskite phases obtained by this methodology and the effects of potassium doping were investigated by the Rietveld method. Changes in the powder morphology, density and weight loss during the sintering process were also studied. Conclusively, potassium does not affect significantly the perovskite amount, but reduces the particle and grain sizes. This dopant also changes the relaxor behavior of 0.9PMN–0.1PT ceramic, reducing the dielectric loss and enhancing the diffuseness of the phase transition.

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1. Introduction

The relaxor-ferroelectric \((1-x)\text{Pb(Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3\) solid solution has attracted considerable attention in the understanding of the structural and physical properties [1]. PMN-based relaxors are characterized by a broad and frequency-dispersive profile of dielectric constant as function of temperature [2,3], being the composition 0.9PMN–0.1PT the most system frequently studied, because the relaxor behavior is not suppressed besides \(T_m\) is shifted toward room temperature [4]. To synthesize PMN–PT single phase is a challenge due the occurrence of the pyrochlore phases that degrade the properties of these materials [5]. Many alternative techniques to synthesize pyrochlore-free PMN-based powders have been developed, but the most successful one is the columbite route [6]. Although this method is able to avoid the preferential reaction between lead and niobium oxides, which is the cause of the secondary phases rising, to synthesize more complex compositions, like the widely used \((1-x)\text{PMN–xPT}\) solid solutions, a new problem has occurred. Substitutions in the B site using the columbite route become very difficult due to the high crystallinity of the columbite structure, which implies in a high chemical heterogeneity in the B site [7].

A good choice is to combine the polymeric precursor method [8] with the columbite route, leading the formation of more reactive powders at lower temperatures than the conventional methods. Furthermore, the insertion of dopants is facilitated due to the use of cation solutions during the powders preparation [9].

In order to optimize the synthesis of 0.9PMN–0.1PT powders, this work purposes a new methodology, which implies in a previous insertion of titanium into the columbite structure using the polymeric precursor method, making the use of additional components (TiO2 or PT) unnecessary, and consequently, a high homogeneity in B site is gotten. It gives a great contribution in the research field, and can be an attractive alternative for industrial manufacture. This new methodology is found on the Ti-modified columbite.
precursor (MN$_{T}$), which shows many potentialities in order to prepare perovskite 0.9PMN–0.1PT powders [10]. The present study was focused in synthesizing potassium-doped 0.9PMN–0.1PT making use of the modified columbite method, investigating the structural effects in MN$_{T}$ and PMN–PT samples, as well the influence on the relaxor behavior and other dielectrics characteristics.

2. Experimental procedure

The modified columbite method was used to prepare three samples of 0.9PMN–0.1PT powders, according to the general formula Pb$(1-x)K_xMg_{0.3}Nb_{0.6}Ti_{0.1}O_{3}$, with $x = 0$, 0.01 and 0.02 (pure, K1-doped and K2-doped samples, respectively). Niobium oxide (Aldrich), basic magnesium carbonate (Cinetica Quimica Ltda), titanium isopropoxide (Fluka) and potassium biphthalate (Vetec) were used to prepare the MN$_{T}$ precursor samples using the polymeric precursor method, as described previously [10]. The final powders were mixed with stoichiometric amount of PbO (Merck), homogenized and heat-treated at 800 °C for 2 h to obtain the perovskite PMN–PT powder samples.

Green bodies with 1.2 cm in diameter were obtained by uniaxial pressing (50 MPa), and prior to sintering, the polyacrylate binder added in the compacting process was burned out at 500 °C for 1 h. The sintered samples obtained by firing at 1100 °C for 4 h in an alumina apparatus [11] were pared (taking of 1–2 mm of the superficial shell) and polished before the silver electrode application.

The MN$_{T}$ precursor, PMN–PT powders and the sintered ceramics were analyzed by X-ray diffraction (XRD) and the data obtained were used for the structural refinement, performed by the Rietveld method. Powders morphology and the microstructures of PMN–PT fractured ceramics were analyzed by scanning electron microscopy (SEM). Measurements of the capacitance and dielectric loss were got at 1, 10 and 100 kHz, using an HP 4192A impedance analyzer.

3. Results and discussion

The XRD patterns of the columbite precursor powders obtained after calcination at 900 °C for 2 h are shown in Fig. 1. All the reflections observed were identified as orthorhombic MgNb$_2$O$_6$ structure, indicating that no secondary phases were segregated in the columbite precursor as consequence of titanium insertion. This result was shown in details in a previous study [10], which focused about the determination of the atomic position occupied by Ti in the columbite structure. In the present work, same results were founded (data not shown), which means that Ti definitively substitutes Mg in the columbite structure.

Regarding the presence of potassium additive in the MN$_{T}$ precursor, it can be seen an enhancement of MN$_{T}$ powder crystallinity, whose effect can be observed by the peak rising at 25.2°, associated to the reflection of the [4 0 0] plane for orthorhombic MgNb$_2$O$_6$ structure, well seen for K2-doped sample. In order to evaluate the effect of potassium in the cell parameters of the columbite structure, a structural refinement was performed and the data are shown in Table 1. Potassium addition causes an increasing in $a$ and $b$ cell parameters, but the reduction in $c$ parameter is more expressive, which makes the unit cell volume decreasing more effectively for 1 mol% than 2 mol% of potassium. It was not possible to define how potassium is inserted into the Ti-modified columbite structure, but we believe that this occurrence is not an ordinary cationic substitution. If so, there should be an increasing in the cell volume due to the large ionic radium of potassium ion, close to 1.64 Å, compared to the ionic radii of MgNb$_2$O$_6$ phase constituents.

The XRD patterns of 0.9PMN–0.1PT powders obtained by the calcination at 800 °C for 2 h are shown in Fig. 2. As can be observed, only the K2-doped sample presents noticeable pyrochlore peak (*), suggesting that amounts beyond 1 mol% of potassium in 0.9PMN–0.1PT composition must be avoided. The data of the perovskite lattice parameter obtained from the Rietveld refinement (Table 1)
shows that a reduction in the molar volume occurs only for K2-doped sample. This becomes the expected potassium substitution in Pb site dubiously, once K+ has ionic radium larger than Pb2+. However, the refinement of the site occupancy factors showed that a slight deficiency of PbO occurs when potassium is inserted into the perovskite structure. For K1-doped sample, the molar volume is not altered because the reduction of the molar volume caused by PbO deficiency is compensated by the enhancement caused by the higher ionic radii of potassium. For K2-doped, the PbO deficiency is more pronounced, resulting in a molar volume reduction and pyrochlore generation. Despite of the Pb site occupancy factor can be reduced in the perovskite structure without the pyrochlore occurrence, if a determined limit for Pb deficiency was overtaking then pyrochlore phase starts to emerge as consequence of the perovskite degrada-

The effect for potassium doping on the sintering process was performed and the representative data are demonstrated in Table 2. The weight loss during the sintering process showed that 1 mol% of potassium avoids the PbO volatilization, but for 2 mol% the same effect was not observed. The pyrochlore presence in K2-doped sample and the high concentration of potassium act probably as barriers for the mass transport, causing a reduction of the ceramic density. Moreover, by SEM characterization (images not shown), it was seen an increasing in the agglomerates size, what affects the powder compacting stage. A satisfactory explanation for these effects can be presented taking in account that in the K-doped 0.9PMN–0.1PT ceramics, the potassium insertion harms the mass transport due to the K–O bond nature, becoming the primary particle size small. Then, there is a diminution in the pores sealing in the initial sintering stage, increasing the weight loss during the beginning of the sintering process and making the composition of the perovskite phase PbO-deficient. Then, the rest of the sintering process gets more difficult, and consequently, the density of the ceramic bulk is reduced.

The understanding of the microstructural phenomena is also very important. Observing the ceramic microstructure for pure (Fig. 3a), K1 and K2-doped ceramics (Fig 3b and c, respectively) it is easy to comprehend these phenomena. The reduction of the grain size and the relation between intergranular and transgranular fractures are function of potassium concentration. In the pure 0.9PMN–0.1PT sample, the grains and its boundaries have approximately the same strength, but when the potassium amount is increased, the average grain size slightly decreases while the fracture mechanism is greatly changed. The fracture mechanism becomes predominantly transgranular indicating that the grains are mechanically weaker than the grain boundaries. Therefore, it can be concluded that the fracture mechanism changes from predominantly intergranular to predominantly transgranular as the potassium is added.

The dielectric properties were also measured for these sintered samples. In Fig. 4 is demonstrated the effect of potassium additive on the dielectric constant and dielectric loss at the frequencies of 1, 10 and 100 kHz. At 1 kHz, the $K_m$ value decreases from 18,000 (Fig. 4a) to 14,000 (Fig. 4b) when 1 mol% of potassium is added to the pure composition and for K2-doped sample (Fig. 4c), $K_m$ goes to 11,000. In addition, potassium additive decreases the dielectric loss around $T_m$. In order to interpret correctly the effect of potassium in the dielectric constant value, the $K_m$ values were corrected considering the relative density of each ceramic (Table 2). The perovskite phase amounts for sintered ceramics after pared and polishing are also shown in this table, besides the values of temperature of maximum dielectric constant ($T_m$) at the frequency of 1 kHz. Considering $K_m$ corrected values, it is possible to determinate that the real decreasing in the dielectric constant around $T_m$ is close to 20%/mol of potassium. In addition, this effect can be attributed to the intrinsic character only, because the high content of perovskite phase was also founded in all sintered samples and it is coherent with the reduction of $T_m$ values (5.4 and 6.8 °C for K1 and K2-doped samples, respectively).

<table>
<thead>
<tr>
<th>Concentration of potassium (mol%)</th>
<th>Perovskite amount (%)</th>
<th>Weight loss (%)</th>
<th>Relative density (g/cm³)</th>
<th>Corrected $K_m$ at 1 kHz</th>
<th>$T_m$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>~100</td>
<td>3.0</td>
<td>96</td>
<td>18,600</td>
<td>21.1</td>
</tr>
<tr>
<td>1</td>
<td>~100</td>
<td>2.8</td>
<td>95</td>
<td>14,480</td>
<td>15.7</td>
</tr>
<tr>
<td>2</td>
<td>99.4</td>
<td>3.9</td>
<td>92</td>
<td>11,540</td>
<td>8.9</td>
</tr>
</tbody>
</table>
The variation of the relaxor behavior can be estimated by determination of the difference between $T_m$ values occurred from 1 to 100 kHz. These $\Delta T_m$ values are shown in Fig. 5 as function of potassium concentration. The addition of potassium enhances the relaxor characteristic of 0.9PMN–0.1PT. It is well known that the relaxor behavior rises from FE/AFE coupling, which is function of alterations in the BO$_6$ octahedra [11]. If the B site containing the ferroelectrically active cations (Nb, Ti) is compressed or expanded, then the FE/AFE coupling can be changed, due to the alteration in the spontaneous polarization $P_s$ of the perovskite structure. For K2-doped sample, the reduction of the molar volume means that B$^{\prime\prime}$ cations are more compressed, which reduces $P_s$ of the structure, and consequently, there is reduction in the ferroelectric behavior of the crystal.

However, for K1-doped sample, a reduction in the molar volume was not observed, in spite of the reduction in the

Fig. 3. Micrographs of 0.9PMN–0.1PT ceramics sintered at 1100 °C for 4 h: (a) pure, (b) K1, and (c) K2-doped.
ferroelectric behavior. This occurrence leads us to suspect that the $P_s$ in the perovskite structure can be changed by other effect, as the BO$_6$ octahedra distortion, originate from the presence of bigger ion in the A site of the perovskite structure. In addition, the strong ionic character of K–O bond can accentuate this distortion.

Other substantial change in 0.9PMN–0.1PT ceramic observed when potassium was added is the diffusiveness of phase transition. The diffusiveness parameter ($\delta$) can be calculated using the following formula [12]:

$$
\frac{1}{K} = \frac{1}{K_m} + \frac{1}{2K_m^2} (T - T_m)^2
$$

where $K$ and $K_m$ are the relative dielectric constant and its maximum value, and $T$ and $T_m$ values are the temperatures corresponding to $K$ and $K_m$, respectively. The data of diffusiveness parameter $\delta$, measured at 1 kHz are shown in Fig. 5 as function of potassium concentration. It is possible to observe that the $\delta$ is greatly enhanced when 1 mol% of potassium is added, while for 2 mol% the $\delta$ is slightly increased. These results can be comprehended considering that potassium lead to a more disordered structure, but the limit of solubility reached between 1 and 2 mol% led to the pyrochlore precipitation. This means that no much more potassium was included into the perovskite phase, which drives to no significant enhance in the diffusiveness of phase transition.

4. Conclusions

Powders of 0.9PMN–0.1PT could be obtained from the modified columbite precursor method free of secondary
phases. The addition of low concentration of potassium avoids the PbO volatilization during the sintering process. The particle and grain sizes were reduced in the additive presence, which were associated to the reducing in the mass transport for 0.9PMN–0.1PT composition. In spite of the decreasing in the dielectric constant for K-doped 0.9PMN–0.1PT ceramics, others interesting results could be presented, such as the reducing of the dielectric loss and enhancement in the relaxor behavior and diffusiveness of the phase transition.

Acknowledgement

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References


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