SYNTHESIS OF FERROELECTRIC PEROVSKITES THROUGH AQUEOUS SOLUTIONS TECHNIQUES

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ABSTRACT

The hydrolysis of niobates in aqueous solutions has been studied as a function of pH and concentration. The process has been applied to the coprecipitation of $PbNb_{2/3}Mg_{1/3}O_3$ leading to a low temperature synthesis of this ferroelectric relaxor ceramic. The effect of hydrolysis conditions such as the concentration of bases and acids used, their rate of addition, temperature and the nature of the precursor salts is described. The homogeneity of the precipitates has been characterized through infrared spectroscopy and X-ray diffraction techniques. The perovskite phase appears after heating at 350°C and is obtained as a pure phase above 750°C after one hour heat-treatment. Relaxor ceramics with high dielectric constant can be obtained by sintering above 1000°C. The process also has been successfully applied to the synthesis of other relaxor ceramic compositions such as PZN ($PbNb_{2/3}Zn_{1/3}O_3$), PFN ($PbNb_{1/2}Fe_{1/2}O_3$) as well as $CdNb_2O_6$ and $MgNb_2O_6$ compounds.

INTRODUCTION

A large number of oxide materials based on niobium crystallize in the perovskite or columbite structure. Lead magnesium niobate (PMN) is a typical example of this family. It is a relaxor ferroelectric perovskite whose high dielectric constant and large electrostrictive coefficient provide interesting applications in the field of capacitors and actuators. However, the dielectric properties of this material are very sensitive to the processing of the ceramic because of the formation of a parasitic phase having the pyrochlore structure [1].

Therefore, more reactive precursors are required in order to favor the formation of the perovskite phase relative to the pyrochlore phase. This can be achieved by a better mixing of Mg and Nb as already described by Swartz and Shrout [2] in their two step process:

$$\begin{aligned} MgO + Nb_2O_5 &\rightarrow MgNb_2O_6 \ (1000°C) \\ 3\ PbO + MgNb_2O_6 &\rightarrow 3\ PbNb_{2/3}Mg_{1/3}O_3 \ (800°C) \end{aligned} \tag{1}$$

A better dispersion of MgO also allows a higher reactivity. Such optimized dispersion can be more easily achieved through the use of solution techniques such as sol-gel processes. However as these processes are mainly derived from alkoxide precursors [3], the high cost and difficulty of handling niobium alkoxides make them useless for the synthesis of bulk ceramics whose applications to capacitors yield a low added value.

In this paper we focus on the use of cheap water solution techniques starting from soluble salts such as potassium orthoniobate (K_3NbO_4), and nitrates or acetates of lead and magnesium.

Niobium species are poorly soluble in water at a pH above 7 whereas magnesium and lead hydroxide precipitate above pH 9.5 and pH 5.5 respectively. We therefore first investigate the appropriate pH for coprecipitation. The principle of our process consists in mixing a basic solution, in which niobate species are soluble, with an acidic solution in which Pb and Mg salts are soluble. The solutions are adapted to yield, upon mixing, a solution of intermediate pH (around 11) allowing coprecipitation of the different combinations of the cations.

The process also has been adapted and successfully tested for the preparation of powders of other compositions such as PZN ($PbNb_{2/3}Zn_{1/3}O_3$), PFN ($PbNb_{1/2}Fe_{1/2}O_3$) and compounds such $CdNb_2O_6$ and $MgNb_2O_6$.

Ceramics have been prepared and their dielectric properties and X-ray diffraction patterns are presented.

EXPERIMENTAL

Preparation and characterization of the solutions

The lead and magnesium solutions have been prepared by dissolving commercial nitrate powders (Prolabo) of the respective elements in water. K_3NbO_4 was chosen as the water soluble niobate compound. It was synthesized by first mixing K_2CO_3 and Nb_2O_5 in the appropriate ratio in a ball mill with ethanol and then reacted by solid state reaction at 740°C during 48h. The reaction must be thoroughly completed in order to avoid later on residual carbonate ions. This compound is easily dissolved in water up to a concentration of 0.3M niobium [4] undergoing the following hydrolysis reaction:

$$6K_3NbO_4 + 10\ H_2O \rightarrow 18K^+ + Nb_6O_{19}^{8-} + 10\ OH^- \qquad (2)$$

The resulting solution thus provides for each niobium 3 basic equivalents where 10x3/18 are OH^- and 8x3/18 are hexaniobate species. This is demonstrated in figure 1a which shows the titration of a 0.3M solution of K_3NbO_4 by HNO_3 1M. Starting at a high pH, OH^- are first titrated and then, the hexaniobate species precipitate into a niobic acid form in a two steps process. A pH as low as 5 is necessary to neutralize all niobate species and no precipitation occurs until the pH decreases down to 11.

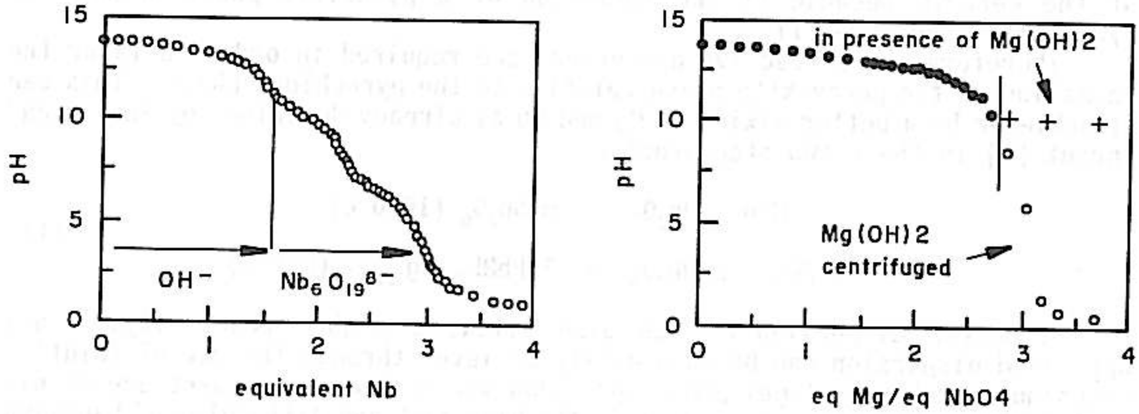

Figure 1. Titration of a 0,3M solution of K_3NbO_4 in water by a) HNO_3 1M b) $Mg(NO_3)_2$ 0,5M.

A slow addition of magnesium nitrate to the orthoniobate solution leads to an immediate precipitation. Because of the presence of $Mg(OH)_2$, which acts as a buffer at pH=10, the solution has to be separated from the precipitate by centrifugation in order to allow the measurement of the final titration (figure 1b). The neutralization point corresponds to a total ratio Mg/Nb=3/2 as can be expected from the precipitation of $5Mg(OH)_2 + Mg_4(Nb_6O_{19})$ species. This means that all niobium can be precipitated by magnesium at a pH above 10.

Titration with lead nitrate yields a similar result although $Pb(OH)_2$ is irreversibly precipitated and does not act as a buffer. However, the amount of lead nitrate solution necessary to titrate the niobate is in excess of the expected 3/2 ratio. This is explained by the fact that the addition of lead nitrate salt to an hydroxide solution leads to the formation of a $Pb(NO_3)_2 \cdot 3Pb(OH)_2$ composition [6]. In other words, not all the lead acts as an acid towards OH and hexaniobate species since some lead is precipitated with its nitrate counterion according to:

$$4Pb(NO_3)_2 + 6\ OH^- \rightarrow Pb(NO_3)_2 \cdot 3Pb(OH)_2 + 6NO_3^- \qquad (3)$$

Upon mixing the niobium, magnesium and lead solutions one obtains a mixture of hydroxides and niobates. Since the amount of Pb and Mg corresponding to the PMN composition can only be precipitated with 4 basic equivalents per each niobium and since 1 K_3NbO_4 only provides 3 basic equivalents, at least one KOH group for each Nb should be theoretically added to the solution of hexaniobates. However, at a too high pH, the niobate species do not precipitate. This is demonstrated by the results of the titration curves obtained with solutions in which different amounts of KOH have been added (table I).

Table I: Titration of niobium loss as a function of the final pH:

KOH added/Nb	2.8	0.85	0.6	0.50
final pH	14	12.6	11.5	10.5
Nb loss	35%	25%	1.5%	0% but loss of 10% Mg

The resulting experiment protocol for the preparation of the PMN composition is therefore the following:

A solution containing the appropriate amounts of both Pb and Mg nitrates (Pb/Mg=3, (Pb)=0.5M/1 for synthesis of PMN) is rapidly added to a niobium solution (Nb=0.3M, KOH=0.15M); the precipitation readily occurs. The precipitate contains some adsorbed potassium hydroxide or nitrate which can be washed out with distilled water. However, the residual potassium species are better washed out after calcination at 750°C as the first process leads also to a relatively high loss of magnesium hydroxide.

Thermal treatment

The progressive crystallization of the material occurs through endothermic weight losses as shown by DSC and TG measurements (figure 2). Typical X-ray diffraction patterns obtained during the calcination process at different temperatures are shown in figure 3. The dried precipitate is essentially amorphous. Upon heating the P_3N pyrochlore phase appears together with small amounts of the perovskite phase (e.g at 350°C). The unwanted P_3N phase starts to diminish around 700-750°C and at 800°C the X-ray pattern is typical of a well crystallized PMN perovskite with traces of a PbO phase.

A similar process has been applied to the preparation of PZN ($PbZn_{1/3}Nb_{2/3}O_3$), PFN ($PbNb_{1/2}Fe_{1/2}O_3$), $CdNb_2O_6$ and $MgNb_2O_6$. In all cases the magnesium nitrate salt has been substituted by nitrates of the respective elements in adequate proportion. As an example the result of the X-ray diffraction of PZN compound is shown in figure 4. The small amount of the PbO phase which is present can be overcome by precise control of the various concentrations of

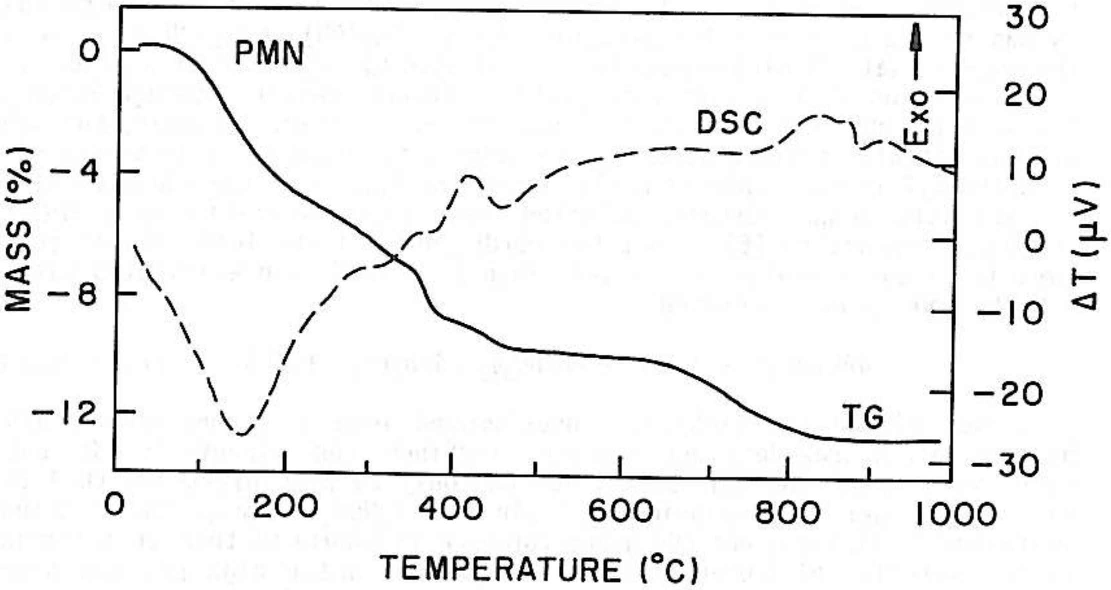

Figure 2. DSC and TG of PMN powder, prepared according to the aqueous process.

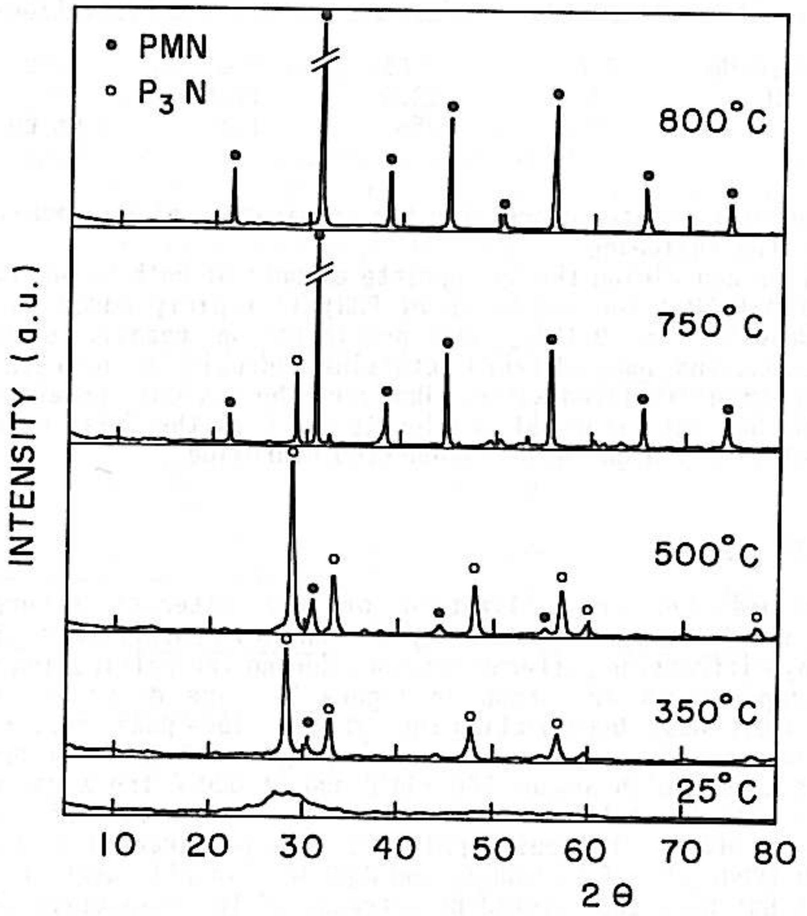

Figure 3. X-ray diffraction patterns of PMN powder measured at 25°C and after heat treatment at 350°C, 500°C, 750°C during one hour respectively.

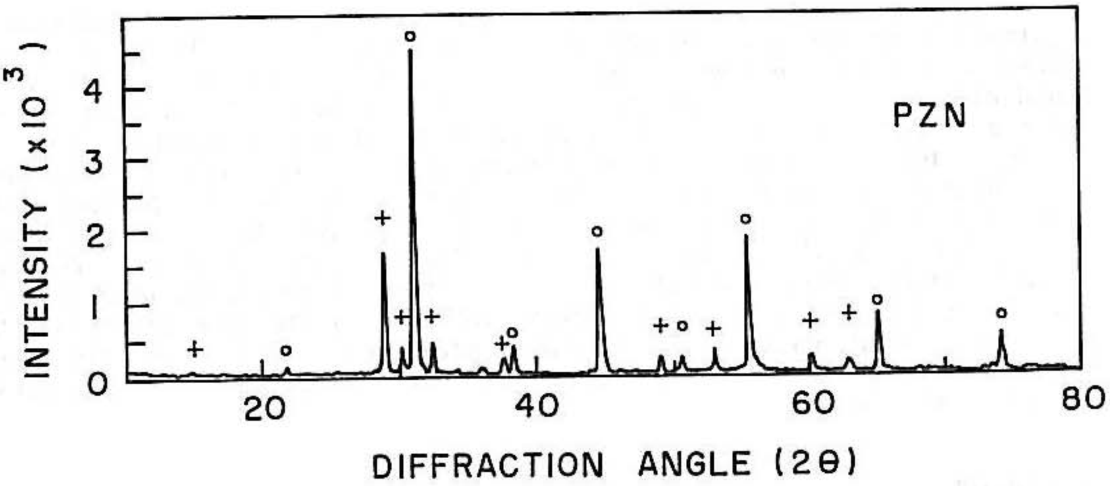

Figure 4. X-ray diffraction pattern of PZN powder calcined at 800°C during one hour (○) PZN, (+) PbO residues.

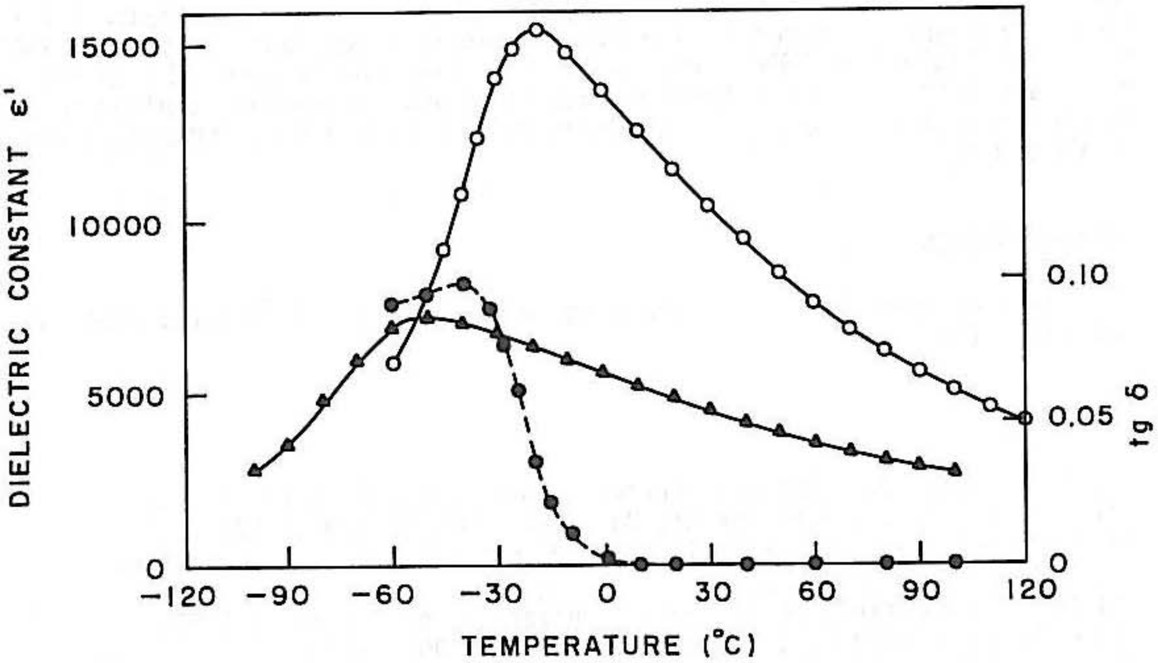

Figure 5. Temperature dependence of the dielectric constant, ε' (○,▲) and dielectric loss, tgδ(•), measured at 1kHz of PMN ceramics sintered at 1050°C during 1h. The materials have been prepared with: (○,•) washed powder, (▲) unwashed powder.

the precursor solutions. On the other hand it is known that PbO acts as a good sintering additive and its presence in small concentration should facilitate the process.

Sintering

A heat-treatment at 800°C for half an hour results in the formation of crystalline PMN powders composed of 2 micron size grains. The powders were washed with water to remove the residual potassium present at the grain boundaries of the structure, dried at 150°C and then pressed into pellets under a pressure of $10t/cm^2$. Finally the material was sintered at 1000°C or higher. Figure 5 shows the dielectric constant and dielectric loss measured as a function of temperature at 1kHz for a pure PMN ceramic obtained after sintering at 1050°C during 1 hour. The curves present the typical behavior of the ferroelectric relaxors with a maximum of the dielectric constant slightly higher than 15000 at 250K. The effect of potassium impurities is drastic as observed with a PMN ceramic sintered in the same conditions but prepared without washing the residual potassium. The lower dielectric constant is attributed to the presence of potassium at the grain boundaries of the structure.

CONCLUSION

A cheap process based on aqueous solutions has been derived for the synthesis of PMN ceramics. The pH is a very important parameter for the control of the composition. A too high pH causes a loss of niobium and a too low pH causes a loss of magnesium. As a result PbO is almost always found in excess in the resulting powders. Potassium ions are also coprecipitated and can be remove by washing the powder before or after calcination. The last process avoids the loss of magnesium by dissolution of magnesium hydroxide in water. For well sintered PMN powder, a dielectric constant as high as 15000 has been obtained at 250K. The presence of potassium drastically decreases the dielectric constant of the ceramics. This process was also applied to the synthesis of other niobate containing materials such as PZN, PFN and niobates of Cd and Mg.

ACKNOWLEDGEMENTS

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REFERENCES

[1] M. Lejeune, J.P. Boillot, Ceramics International, 8 (1982) 99.
[2] S.L. Swartz and T.R. Shrout, Mat. Res. Bull 17 (1982) 1245.
[3] H.U. Anderson, M.J. Pennell and J.P. Guha, Advances in Ceramics, 21 (1987) 91.
[4] G. Guzmàn-Martel, Ph.D. Thesis, University of São Paulo (1991)
[5] M.T. Pope and B.W. Dale, Quart. Rev. 22 (1968) 527
[6] J.L. Pauley and M.K. Testerman, J.Am. Chem. Soc. 76 (1954) 4220.