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Piezoelectric and optical properties of Sr-doped PT–PZ–$Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramics

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Abstract

Ceramics in the ternary system $(Pb,Sr)TiO_3$–$PbZrO_3$–$Pb(Mg_{1/3}Nb_{2/3})O_3$, in the ratio 85.976/5.817/8.207 mol%, was prepared by mixed oxide route. With about 13.98 at.% Sr^{+2}, as isovalent substitution in A-position of the lead titanate, high-density samples were obtained for the sintering temperatures of about 1220 and 1230 °C. Tetragonal phases were identified both by XRD method and selected area electron diffraction pattern (SAED). The lattice parameter ratio, c/a, of about 1.017 indicated a decrease of tetragonal distortion. The typical TEM micrographs showed domains of about 50 nm wide. The reflection spectra were recorded to prove the presence of the transition Ti^{+4} to Ti^{+3}. The principal mechanical, electrical and electromechanical properties were discussed as a function of the sintering temperature. The variation of the relative constant with the temperature and frequency evidenced a relaxation-like behavior of this ternary system. By combining the ferroelectric and relaxor end member we tried to improve the piezoelectric properties of a ceramic with a high content of lead titanate, and to achieve a material with both piezoelectric and relaxor-like properties.

Keywords: Dielectric properties; Microstructure; Optical properties; Relaxors; Titanates

1. Introduction

The unmodified lead titanate is an ABO_3-type compound with a tetragonal structure at room temperature. The distortion of $PbTiO_3$ unit cell is about 1.063, much greater than in $BaTiO_3$. The lattice parameters vary with the temperature and hydrostatic pressure. Pure $PbTiO_3$ (PT) cannot be used as a material for piezoelectric transducers, but with various substitutions (isovalent-, compensating valence- and A-vacancy substitutions), new materials with piezoelectric properties were obtained. Sr^{+2}, as isovalent substitution for Pb^{+2} in PT, decreases the Curie point of the ceramic and reduces the tetragonal c/a ratio. A Curie point of about 180 °C is reported for a PT composition with 50 at.% Sr^{+2}. Is important to remark that for compounds with high concentration in Pb^{+2} and small content in Sr^{+2}, no piezoelectric properties have been reported.

Strong piezoelectric effects are observed for $PbTiO_3$ modified with other compounds, near the morphotropic phase boundary, where co-exist both rhombohedric and tetragonal phases. The composition of the morphotropic phase is specific for each compound or substituent added to lead titanate. The molar content of PT varies from 5–6 mol% to 35 mol% and 47–48 mol% for the PT–$Pb(Fe_{0.5}Nb_{0.5})O_3$, PT–$Pb(Mg_{1/3}Nb_{2/3})O_3$ and PT–$PbZrO_3$, respectively. For these compositions large planar coupling factors of nearly 0.6 and dielectric constant over 3000 have been reported. Many studies are made on the piezoelectric properties of binary and ternary systems near the morphotropic phase boundary, with the PT maximum content of about 48–50 mol%.[1,2] None studies were reported concerning ternary systems with a PT content more than 80 mol%.

The aim of this contribution is to study a ternary system composed from lead titanate, lead zirconate and $Pb(Mg_{1/3}Nb_{2/3})O_3$, with a high content of PT, more than 85 mol%. We have chosen a mixture of about 85.976 mol% Sr^{+2}-modified PT and 5.817 mol% $PbZrO_3$ (PZ), far from the morphotropic phase boundary in the PT–PZ phase diagram, with an unique ferroelectric tetragonal phase. In the lead titanate, 13.98 at.% Pb^{+2} were isovalent substituted with Sr^{+2}. At the above mixture we added 8.207 mol% $Pb(Mg_{1/3}Nb_{2/3})O_3$, a well-known relaxor compound, in order to improve the piezoelectric properties of the system. The principal mechanical, electrical and electromechanical properties

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were determined as a function of the sintering temperature. Using transmission electron microscopy (TEM) and X-ray diffraction method we have investigated the microstructure of the sample sintered at 1220 °C. The ternary system contains a high concentration in Ti^{+4} together with, as additives, both isovalent ions (Sr^{+2}, Mg^{+2}) for Pb^{+2} substitution and donor ions (Nb^{+5}) for Ti^{+4} substitution. For this reasons it is expected that Ti^{+4} can reduce to Ti^{+3} in order to compensate Nb^{+5}. For evidencing this transition, reflection spectra were recorded. The presence of the niobate member of the ternary system will induce a relaxation-like behavior, so the dependence of the relative dielectric constant with the temperature and frequency was studied.

2. Experimental

A ternary mixture with the composition $Pb_{0.8611}Sr_{0.1389}TiO_3/PbZrO_3/Pb(Mg_{1/3}Nb_{2/3})O_3$, in the ratio 85.986 mol%/5.817 mol%/8.2068 mol%, have been prepared from reagent grade oxide and carbonates via a solid-state reaction method. Nickel electrodes were chemically deposited on the pellets sintered in the temperature range of 1180–1230 °C.[3] The samples were poled in a silicon oil bath at 220 °C under an electric field of 3 kV/mm. Densities were estimated by Archimedes's method. For the investigation of the crystallographic system, unit-cell parameters were determined from X-ray diffraction (XRD) patterns, on a Seifert installation. The transmission electron microscopy (TEM) study was performed on specimens prepared by grinding fragments of the ceramic pellet into fine powder. We used a Jeol 200CX instrument operated at 200 kV. The reflection spectra were measured on an experimental set up composed by a source of light, a monochromator, a photomultiplier and an acquisition data system. The sample is positioned at 45° to the incident light. The reflection was corrected using a $BaSO_4$ white standard. The dielectric and piezoelectric properties were determined by means of resonance–antiresonance method, using a HP 4194A Impedance gain/ phase Analyser, 24 h after poling. The microstructure, the optical, the piezoelectric and the dielectric properties of the material are correlated with the sintering temperature of the samples.

3. Results and discussion

3.1. Microstructure

The samples were first analyzed by X-ray diffraction using a Seifert installation. The XRD spectrum of a sample sintered at 1220 °C, shown in Fig. 1, reveals the formation of a well-crystallized ceramic. The diffraction peaks were identified and showed the presence of a unique crystalline phase with the stoichiometric formula $Pb_{0.95}Sr_{0.05}(Ti_{0.36}Zr_{0.265}Mg_{0.125}Nb_{0.25})O_3$,. The peaks were indexed in the tetragonal system and the calculated parameters are $a=b=0.401$ nm and $c=0.408$ nm. However, the spectrum contains some other diffraction peaks located at 25.7 and 29.1°, suggesting traces of non-reacted precursor oxides, such as TiO_2 (brookite) and Nb_2O_5, respectively.

The transmission electron microscopy (TEM) image, shown in Fig. 2a, illustrates a typical grain of about 450 nm resulted from the preparation procedure. The crystal grain is characterized by a typical contrast (dark fields) proving the existence of lattice strain. The grain is made of elongated domains visible as stripes of about 50 nm wide. The corresponding selected area electron diffraction (SAED) pattern is presented in Fig. 2b and confirms the formation of a well-crystallized tetragonal phase, as already shown by the XRD spectrum. As one can see from the spot doubling, the diffraction pattern is the result of the superposition of two diffraction patterns, along the same [001] zone axis corresponding to domains rotated at 85° from each other. The rotation angle between the domain walls can be measured on the SAED pattern, as well as on the TEM image.

3.2. Principal properties

The optical, mechanical, electrical and electromechanical properties of the material are studied as a function of the sintering temperature and are presented in the Figs. 3–9. Unexpected good piezoelectric properties have been obtained for a material with a high content of titanium (more than 85 mol%), and a composition far from the morphotropic phase boundary.

3.3. Optical properties

Optical spectra represent sources of information regarding the transitions of the ions in a material. The absorption spectra are used for the investigation the transparent media, while the diffuse reflectance spectra are used for the powered and non-transparent samples.[4]

In this particular ternary solid system, we investigate the electronic transitions due to titanium ions, observed in the reflection spectra.

Ti has a $3d^24s^2$ configuration and no absorption contribution is expected for Ti^{+4} ions. The valence decrease of Ti^{+4} to Ti^{+3} ($3d^2$), or Ti^{+2}($3d^1$) is taken into consideration to explain absorptions in the spectra. The Ti^{+2} ions transitions in the crystal field approximation are the following: $^3T_{1g}(P)\leftarrow{}^3T_{1g}$, and $^3A_{2g}\leftarrow{}^3T_{1g}$; a large absorption band was reported at about 650 nm. For the Ti^{+3} ion, $^2B_{1g}\leftarrow{}^2B_{2g}$ and $^2A_{1g}\leftarrow{}^2B_{2g}$ are the

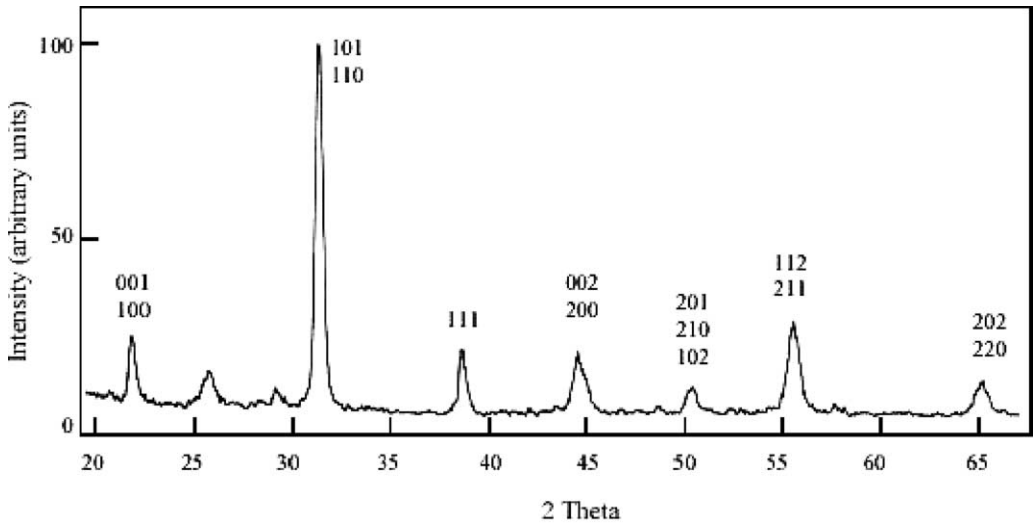

Fig. 1. X-ray diffraction pattern of PT–PZ-niobate type material substituted with Sr.

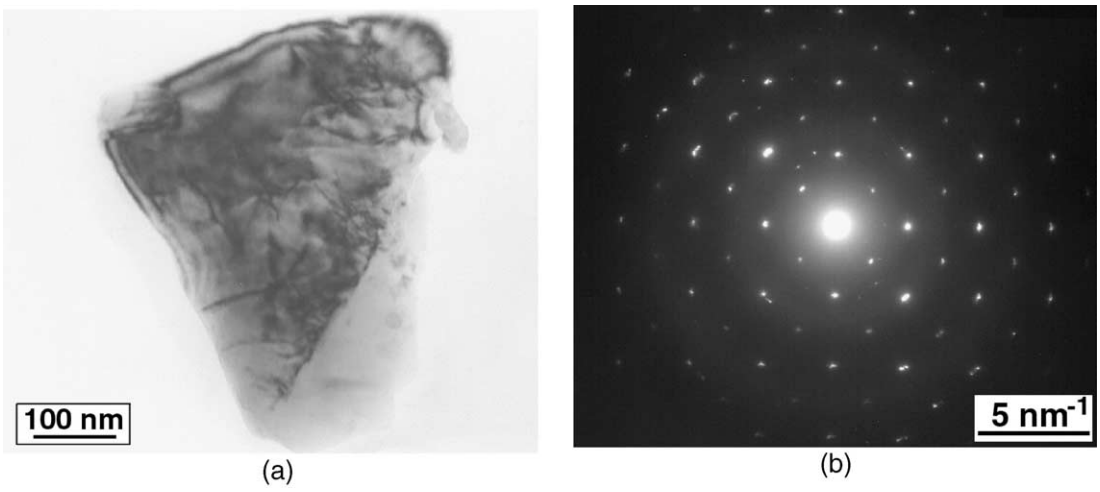

Fig. 2. (a) TEM image of a sample sintered at 1220 °C; (b) SAED pattern of a sample sintered at 1220 °C.

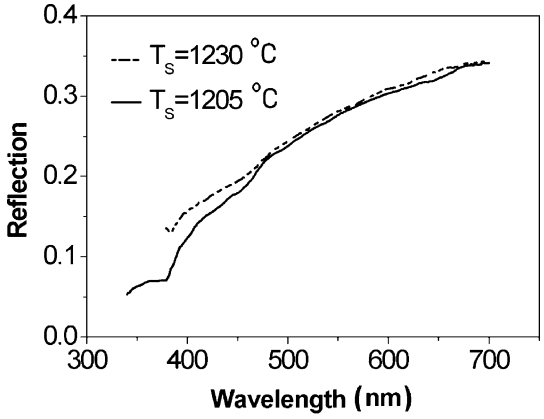

Fig. 3. Optical reflectance spectra of the samples sintered at 1205 and 1230 °C.

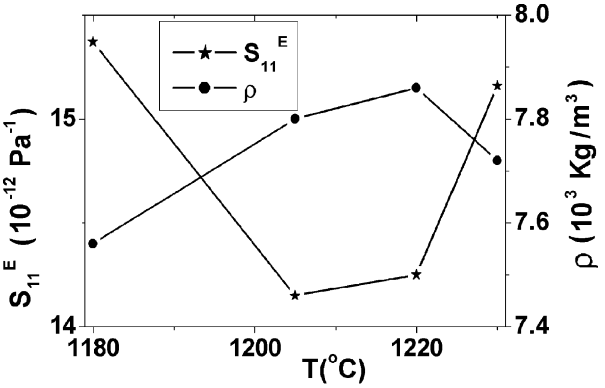

Fig. 4. The compliance S_{11}^{E} and density vs. the sintering temperature.

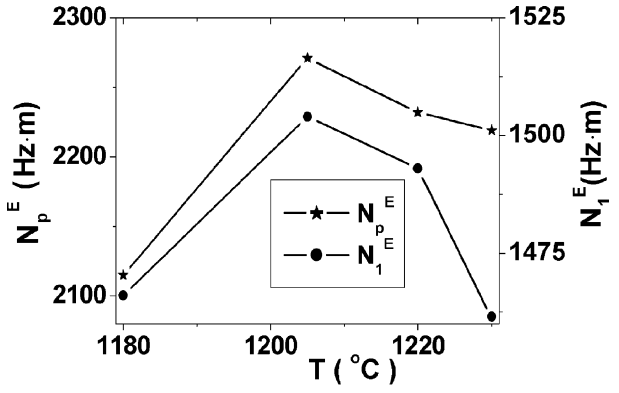

Fig. 5. The frequency constants, N_p^E and N_1^E, vs. the sintering temperature.

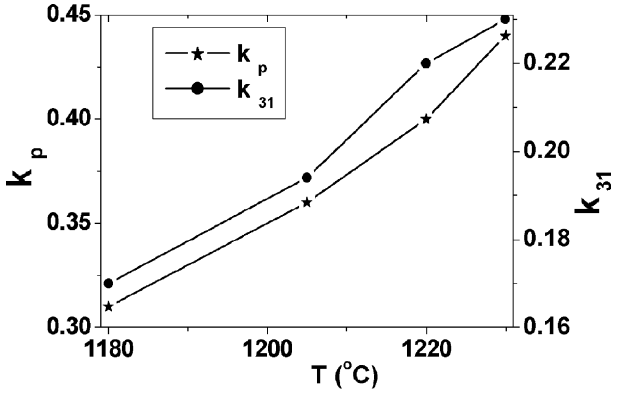

Fig. 6. The electro-mechanical coupling factors k_p and k_{31} vs. the sintering temperature.

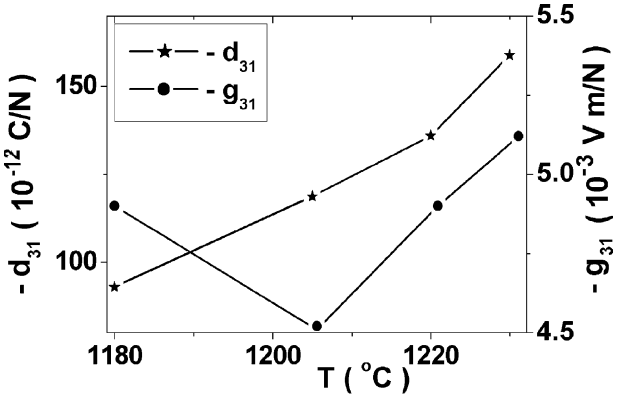

Fig. 7. The piezoelectric charge constant d_{31} and the piezoelectric voltage constant g_{31} vs. the sintering temperature.

transitions in the tetragonal field, with a large absorption band at about 550 nm.[4]

An increase of absorption bands intensity attributed to Ti^{+3} and Ti^{+2} transitions for the PT–PZ-niobate samples prepared at two sintering temperatures 1205 and 1230 °C, is observed in Fig. 3. These bands are located at about 640 and 535 nm, respectively. At both sintering temperatures, Ti^{+3} is present in the samples, while Ti^{+2} seems to be present only in the sample

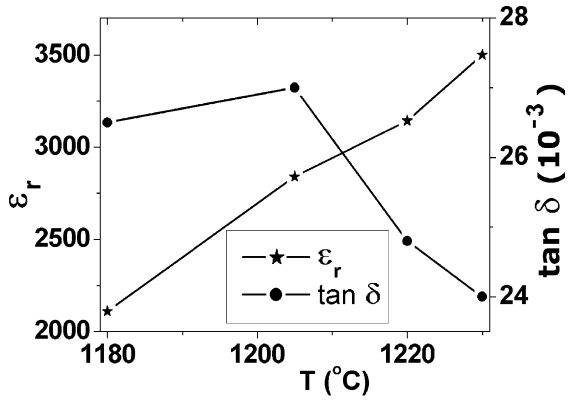

Fig. 8. The variation with the sintering temperature of the relative dielectric constant and the dielectric loss factor.

sintered at the lower temperature. The volatilization of lead oxide has been prevented during sintering process by embedding the pressed samples in a grounded powder with the same composition. One can suppose that the stoichiometry of the system is maintained by valence change from Ti^{+4} to Ti^{+3}, like in $BaTiO_3$. On the other hand, the replacement of Ti^{+4} by Nb^{+5} might induce the reducing of Ti^{+4} to Ti^{+3} in order to compensate the Nb^{+5}.

Further investigations are necessary for the explanation of the presence of Ti^{+2}.

3.4. Mechanical data

The maximum density of about 7.86 g cm^{-3} was obtained for a sintering temperature of 1220 °C. The compliance values are between 14.15 and $15.16 \cdot 10^{-12}$ Pa^{-1}; the mechanical quality factor for the radial mode, Q_m^E, decreases from 84 to 68 with the increase of the sintering temperatures from 1180 to 1230 °C. The mean values of the frequency constants N_p^E and N_1^E are about 2230 and 1470 respectively.

3.5. Electro-mechanical data

The maximum value of k_p obtained for our system is only 0.44, but is the best value reported for a material with a very high content in lead titanate. The piezoelectric charge constant d_{31} and the piezoelectric voltage constant g_{31} are of about $-150 \cdot 10^{-12}$C/N and -5×10^{-3} Vm/N, respectively.

3.6. Electrical data

The dielectric constant values and dielectric loss factor, tan δ, versus the sintering temperature are shown in Fig. 5. The relative dielectric constant increases linearly up to a value of over 3500. For the samples sintered over 1220 °C, the dielectric loss factor of the material is about $25 \cdot 10^{-3}$.

In order to measure the temperature induced phase transitions, the series capacity versus temperature was

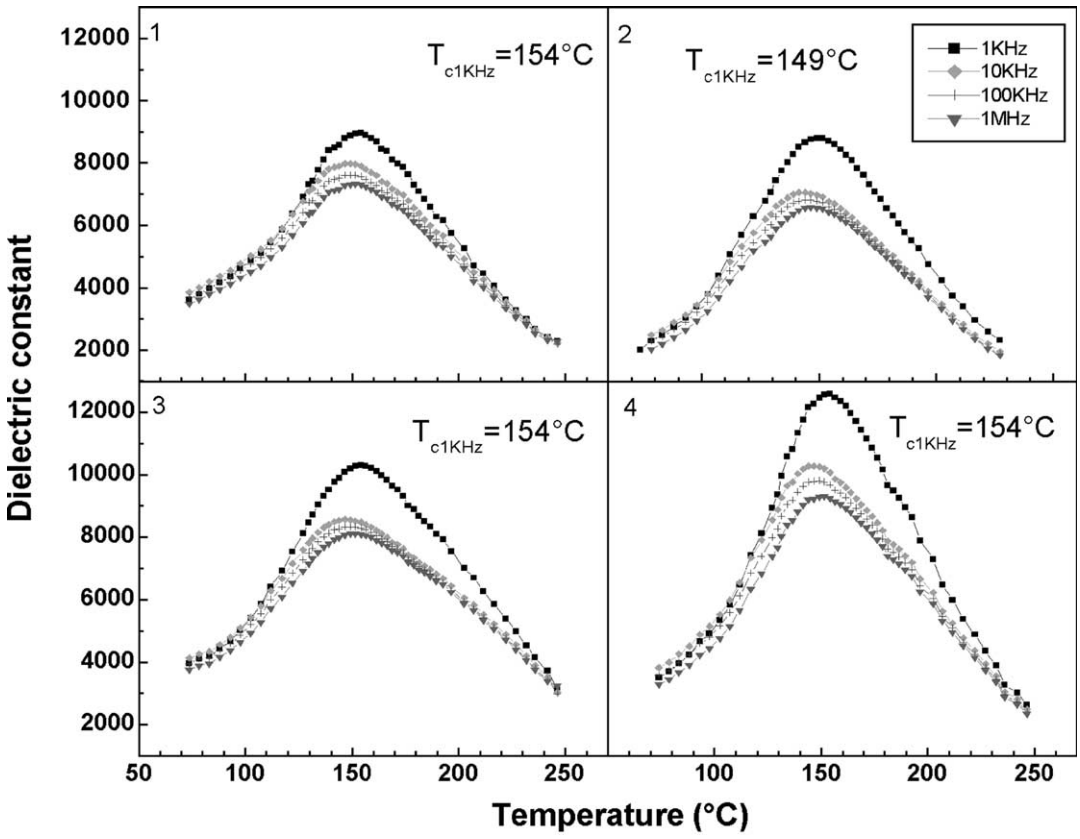

Fig. 9. Temperature dependence of the relative dielectric constant of the material sintered at: (1) 1180 °C; (2) 1205 °C; (3) 1220 °C; (4) 1230 °C.

measured at several frequencies of 1 kHz (standard), 10 kHz, 100 kHz, 1 MHz. This was done by heating the sample into an electric furnace and measuring the temperature and the series capacity. An impedance analyzer type HP 4194 A was used for the series capacity measurements. In order to minimize the errors, automatic measurements have been preferred. The real part of the dielectric constant was computed from the geometry of the samples.

The temperature and frequency dependence of the real part of the relative dielectric constant of the samples sintered at several temperatures is shown Fig. 9. Curie temperatures of about 154 °C are measured. The Sr^{+2} for Pb^{+2} substitution could be the one of the reason for the low value of the Curie temperature. The value of the peak is frequency dependent and its Curie temperature is shifted towards smaller temperatures. The broad peaks can be associated with a relaxor phase.

The studied ternary system is a complex one. The small amounts of lead zirconate and $Pb(Mg_{1/3}Nb_{2/3})O_3$ added to over 85 at.% lead titanate are beneficial to the system. Even the system is far from the morphotropic phase boundary the piezoelectric properties of the lead titanate are improved. High dielectric constant of about 3500 are measured, and a relaxation process is observed.

It would be possible to obtain higher piezoelectric properties for such systems containing *PT* of a majority, with other amounts of lead zirconate and $Pb(Mg_{1/3}Nb_{2/3})O_3$.

Further experiments are necessary to correlate the amount of Ti^{+2} and Ti^{+3} with the dielectric and piezoelectric properties of the samples and to elucidate the mechanism of the conduction processes in our ferroelectric ternary system.

4. Conclusion

Unusually high piezoelectric and dielectric properties were obtained for a ternary system composed from: $(Pb,Sr)TiO_3$–$PbZrO_3$–$Pb(Mg_{1/3}Nb_{2/3})O_3$, with a content in *PT* over than 85 mol%. Ferroelectric tetragonal phases were identified by XRD method, with a lattice parameter ratio, c/a, of about 1.017. Optical reflection spectra in visible region reveal transition of titanium from +4 to +2 and +3. The relative dielectric constant increases linearly up to a value of about 3500 with the sintering temperature. The broad peaks of relative dielectric constant, and the dependence of the peaks with the frequency can be associated with a relaxor phase. The relaxation-like behavior may be attributed to some disorder induced by the following factors: (a) the presence

of the compound $Pb(Mg_{1/3}Nb_{2/3})O_3$; (b) the Sr^{+2} substitution for Pb^{+2}; (c) titanium transitions.

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