Structural and dielectric studies of ferroelectric or relaxor ceramics in the Ca$_{1-x}$Na$_x$ (Ti$_{0.5}$Sn$_{0.5}$)$_{1-x}$ Nb$_x$O$_3$ system

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Abstract

New ternary lead free CaSnO$_3$–CaTiO$_3$–NaNbO$_3$ (CSNNT$_x$) ferroelectrics were prepared by a solid-state reaction method. The X-ray diffraction patterns at room temperature revealed a single phase perovskite crystallizing with cubic Pm3m group symmetry for $x \geq 0.8$ and in tetragonal group P4mm for $x \leq 0.8$. The real part of the relative dielectric permittivity ($\varepsilon'_r$) exhibited a sharp peak with no frequency dependence which revealed a classical ferroelectric behavior for some compositions and ferroelectric relaxor behavior for others, with a diffuse phase transition and frequency dispersion. The ferroelectric behavior has been confirmed by hysteresis investigation. Raman spectra at room temperature shows a disorder introduced in this composition, thus favoring a ferroelectric relaxor behavior.

$\varepsilon'_r$ (13613–13613)

Keywords: Ceramic; Ferroelectric; Dielectric; Relaxor; Raman

1. Introduction

Due to their wide range of applications with regard to high performance materials and their dielectric, electromechanical and pyroelectric properties, ferroelectric compounds have been studied in much detail [1–2]. According to their behavior, ferroelectric materials may be divided into two different classes, namely classical or relaxor ferroelectric compounds, depending on the temperature and frequency variations of the real part of the permittivity [3]. The best known relaxor is Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$, a lead-based ceramic with perovskite structure. In accordance with environmental concerns, we have avoided PbO-related problems; thus researchers have moved toward lead-free relaxor [4]. The effect was then related to the substitution within octahedral site in lead free perovskite which is related either to a cationic or anionic disorder in A or B sites of ABO$_3$ structure [5–8].

Pure NaNbO$_3$ is antiferroelectric at room temperature, with orthorhombic distorted perovskite structure with a space group Pbnm and a Curie temperature of 360 $^\circ$C. It easily becomes ferroelectric by low rate substitutions [9–13]. The crystal structure of the CaSnO$_3$ is a paraelectric perovskite [14]. It is useful for application as thermally stable capacitor in dielectric industries due to their attractive dielectric characteristics [15–16]. CaTiO$_3$ is an ABO$_3$ perovskite type with displacive ferroelectric properties [17–18].

Recent studies reveal the potentially interesting properties of these materials as thermally stable capacitors with low permittivity. It is well-known that a suitable substitution on different atomic sites induces important modifications in the electric and structural properties of Ca$_{1-x}$Na$_x$ (Sn$_{0.5}$Ti$_{0.5}$)$_{1-x}$Nb$_x$O$_3$ [19]. Therefore, it is of great interest to study the effect of the substitution of Ca by Na and (Ti, Sn) by Nb in NaNbO$_3$ perovskite. We have synthesized and studied various properties of the new ceramic compound, with the general formula Ca$_{1-x}$Na$_x$ (Ti$_{0.5}$Sn$_{0.5}$)$_{1-x}$Nb$_x$O$_3$ ($x=0.6; 0.7; 0.8; 0.9$), which is simplified by the expression CSNNT$_x$. As a result, we were able to present...
the SEM, crystallographic, dielectric, hysteresis and Raman of CSNNTx ceramics.

2. Experimental procedure

The polycrystalline samples of Ca$_{1-x}$Na$_x$(Ti$_{0.5}$Sn$_{0.5}$)$_{1-x}$Nb$_x$O$_3$ with $x = 0.6; 0.7; 0.8$ and $0.9$ were prepared by a solid state reaction technique. The starting powders CaCO$_3$, Na$_2$CO$_3$, Nb$_2$O$_5$, TiO$_2$ and SnO$_2$ were mixed in agate mortar for 1 h, and calcined in oxygen atmosphere at 1150 °C for 15 h. After calcinations, powders have been mixed for 1 h and pressed under 100 MPa into disks of 8 mm in diameter and about 1 mm in thickness. Finally, the formed pellets have been sintered at 1250 °C for 2 h under an oxygen rich atmosphere. The diameter shrinkage, $\frac{\phi_{\text{int}}}{\phi_{\text{final}}}$, and the compactness $\frac{\rho_{\text{exp}}}{\rho_{\text{th}}}$ (experimental density/theoretical density) were systematically determined, and their average values were 0.16 and 92%, respectively.

The X-ray diffraction analysis, at room temperature, were recorded on a Philips diffractometer using the CuKα radiation in the angular range $27^\circ \leq 2\theta \leq 81^\circ$ with a 0.02° steps and a counting time of 10 s. This made it possible to verify that the samples were single phase. The scanning microscope (SEM), JEOL 6360 A, which was used to characterize the microstructure, shows that the sample is well densified [20].

The dielectric measurements were performed on ceramic disks after the deposition of gold electrodes on the circular faces by cathodic sputtering. The real parts of permittivity were determined under dry helium as a function of both temperature (80–700 K) and frequency (0.1–200 kHz) ranges using a Wayne-Kerr 6425 analyzer component [21]. A Sawyer-Tower circuit was used to measure the polarization hysteresis ($P$–$E$) loop at room temperature [22]. The Raman spectra were recorded on a Horiba Labram 800 instrument using the 514.5 nm exciting light of argon laser.

3. Results and discussions

3.1. X-ray diffraction analysis

The XRD patterns were analyzed to confirm the symmetry and calculate the lattice parameters for Ca$_{1-x}$Na$_x$(Ti$_{0.5}$Sn$_{0.5}$)$_{1-x}$Nb$_x$O$_3$ (CSNNTx) compound with $x = 0.6; 0.7; 0.8$ and $0.9$ samples. The values of the lattice and profile parameters were determined using a global profile matching method with the software “Fullprof” [23]. All the reflection peaks of the X-ray profiles were indexed with only one perovskite-type phase. The observed and calculated XRD patterns of ceramics and the difference between them, with composition $x = 0.7$ and $x = 0.8$, are shown in Fig. 1a and b as examples. The symmetry of the ceramic specimens appears to be cubic with Pm3m group symmetry for the compositions in the range $x < 0.8$ and tetragonal with P4mm group symmetry for compositions in the range $x \geq 0.8$.

![Fig. 1. (a) X-ray diffraction pattern of a CSNNTx powder with composition corresponding to $x=0.7$. (b) X-ray diffraction pattern of a CSNNTx powder with composition corresponding to $x=0.8$.](image)

![Fig. 2. Variation of unit cell volume with x composition.](image)
The variation of the unit cell volume with x composition is plotted in Fig. 2. The decrease of the lattice parameters can be due to the substitution of the sodium and the niobium by the calcium and the (Ti, Sn), respectively. The decrease in the volume with the increase of x can be due to the values of ionic radii $r$ ($\text{Na}^+ = 1.18 \, \text Å$) and $r$ ($\text{Nb}^{5+} = 0.64 \, \text Å$) for NaNbO$_3$, which are quite lower than those of $r$ ($\text{Ca}^{2+} = 1.18 \, \text Å$), $r$ ($\text{Sn}^{4+} = 0.69 \, \text Å$) and $r$ ($\text{Ti}^{4+} = 0.61 \, \text Å$) for Ca (Sn, Ti) O$_3$.

3.2. Scanning electron microscope (SEM)

The SEM micrograph of CSNNT0.8 ceramic sintered at 1250 °C for 2 h is shown in Fig. 3. We obtain a ceramic with a bulk density reaching 90% of the theoretical value. The grain size is about 2 μm. It is worth mentioning that high performance materials with high density and uniform microstructure could only be achieved if both composition and grain growth are controlled.

3.3. Dielectric studies

The evolution of the real part of dielectric permittivity ($\varepsilon_r'$) of the ceramic samples as a function of temperature at various frequencies (0.1–200 kHz) of CSNNTx (0.6 ≤ x ≤ 0.9) was determined. Two different dielectric behaviors were observed.

For $x < 0.8$, there was only one broad peak at $T_m$ (the temperature of maximum permittivity) in the thermal evolution of $\varepsilon_r'$. A frequency dispersion occurred for $T < T_m$ with a shift of $T_m$, with frequency evolution. Fig. 4a and b shows the temperature dependencies of the real parts of permittivity $\varepsilon_r'$ at different frequencies of the sample with composition $x = 0.6$ and 0.7. Diffuse transition with frequency dispersion above and around the $\varepsilon_r'$ peak was observed. The temperature $T_m$ of $\varepsilon_r'$ (maximum) shifted to higher values with the increase of frequency and decrease of intensity of $\varepsilon_r'$. In our case, the evolution of the frequency dispersion was characterized by a decrease in $\varepsilon_r'$ when frequency increased. This shows that these compositions are of a relaxor type.

For $x ≥ 0.8$, the permittivity evolution shows classical ferroelectric behavior. For example, Fig. 5a and b shows the temperature dependence of the real part of the permittivity $\varepsilon_r'$ at several selected measurement frequencies from 0.1 to 200 kHz, for $x = 0.8$ and 0.9 samples. The maximum of the permittivity at the ferroelectric–paraelectric phase transition, $T_C$, does not vary with frequencies. We note that there is no significant frequency dispersion for $T > T_C$.

The variation of the temperature of dielectric anomalies as a function of composition $x$ is shown in Fig. 6. It can be observed that the value of $T_m$ or $T_C$ increases with the increase in $x$, and the relaxor character becomes more important with its decrease. This behavior is then similar to those reported in the literature [24].

The relaxor behavior in our ceramics can be explained by the strong heterogeneity introduced in NaNbO$_3$ by Ca and (Ti, Sn). These results have demonstrated that the introduction of the solid solution CaSnO$_3$–CaTiO$_3$ in NaNbO$_3$ causes the decreases of $T_m$ when $x$ decreases.

Furthermore, the dielectric constant of a normal ferroelectric in the paraelectric region is generally known to follow the Curie–Weiss law described by the following equation:

$$\varepsilon_r' = \frac{C}{(T-T_C)}, \quad T > T_C$$

(1)

where $T_C$ refers to the Curie temperature and C to the Curie–Weiss constant. Fig. 7 shows the variation of the inverse dielectric constant $1/\varepsilon_r'$ as a function of temperature at 1 kHz.
The experimental data were fitted by Eq. (1) using a nonlinear curve-fitting method.

The value of $T_C$ is very close to the Curie–Weiss temperature $T_0$, which implies that the phase transition is clearly of the second order and the ferro-electricity is of a classical type [25,26].

Uchino and Nomura [27] have previously proposed a modified Curie–Weiss law to describe the diffuseness of the phase transition as follows:

$$\left(\frac{1}{\varepsilon'_m} - \frac{1}{\varepsilon'_r}\right) = \left(\frac{T - T_m}{T_0}\right)^\gamma$$

(2)

where $\gamma$ and $C_1$ refer to the modified constants, with $1 < \gamma < 2$. The value of the parameter $\gamma$ gives information about the nature of the phase transition. The value of $\gamma$ is 1 for the case of a classical ferroelectric, and a cubic (i.e. $\gamma=2$) is valid for an ideal relaxor ferroelectric [28,29]. The deviation for $T < T_{\text{dev}}$ is a characteristic of dipole interactions responsible for some type of short-range order. The large curvature of $1/\varepsilon'_r$ around $T_m$ in Fig. 8 is in good agreement with a strongly diffused phase transition.

The value of Curie–Weiss temperature $T_0$ was greater than that of $T_m$. However, a deviation from the Curie–Weiss was observed. The degree of deviation can be defined as $\Delta T_m = T_{\text{dev}} - T_m$, where $T_{\text{dev}}$ denotes the temperature from which ($\varepsilon'_r$) starts to deviate from the Curie–Weiss. $T_m$ represents the maximum of temperature. These parameters are $T_m = 95$ K, $T_0 = 113$ K, $T_{\text{dev}} = 213$ K and $\Delta T_m = T_{\text{dev}} - T_m = 119$ K. Actually, $\Delta T_m$ is a very important equaling 119 K, which makes its compositions (in the family of relaxor) useful for applications.

Logarithmic plots related to this equation for the composition $x=0.7$ is shown in Fig. 9. The slope of the curve gives the value of $\gamma$ at 10 kHz. This parameter is $\gamma=1.75$, for $x=0.7$. The value of $\gamma$ shows that the materials are highly disordered.

The relaxor behavior can be induced by many reasons such as a microscopic region, the merging of micropolar regions into macro polar regions [30], local compositional fluctuation [31], superparaelectric [32], and dipolar glass model [33]. In our solid solution Ca$_{0.3}$Na$_{0.7}$Sn$_{0.5}$Ti$_{0.5}$Nb$_{0.7}$ O$_3$, Na$^+$ and Ca$^{2+}$ ions co-occupy the A-site of ABO$_3$ perovskite structure, and Nb$^{5+}$ and Sn$^{4+}$ and Ti$^{4+}$ ions co-occupy the B site. Therefore, the cations disorder in perovskite unit cell should be one of the reasons for the appearance of relaxor state. On the other hand, it is known that the NaNbO$_3$ (NN) is antiferroelectric at room temperature [34]. The partial heterogeneous substitution of NN by Ca(Sn$_{0.5}$Ti$_{0.5}$)O$_3$, $x=0.7$ make these ceramics ferroelectric.

The frequency dispersion of the $\varepsilon'_r$ in relaxor ferroelectrics has been attributed to the distribution of relaxation times. A large number of theoretical models have been proposed to understand the diffusiveness and dispersion. The Vogel–Fulcher model has been considered as the most successful mathematical representation for the divergent nature of relaxation time below certain temperature [35]. The observed frequency dependence of $T_m$ was empirically evaluated using Vogel–Fulcher’s relationship given as:

$$f = f_0 \exp \left[ \frac{-E_a}{Kb(T_m - T_i)} \right]$$

where $f$, $E_a$, $T_i$ and $f_0$ are applied frequency, activation energy, freezing temperature and attempt frequency, respectively. In our case, the compositions $x=0.6$ and $x=0.7$ obey this
relation. In Fig. 10, we present the variation of \( \log f \) as a function of \( T_m \) for \( x=0.7 \) as an example. The parameters of the obtained Vogel–Fulcher relation are \( E_a=0.051 \text{ eV}, \ f_0=3.1 \times 10^4 \text{ Hz} \) and \( T_i=130.01 \text{ K} \).

The temperature of the maximum of the real part of the dielectric permittivity \( T_m \) can be related to the frequency by the phenomenological Vogel–Fulcher relation [36]

\[
\log f = \log f_0 - \frac{E_a}{K(T_m - T_i)}
\]

where \( f_0 \) is the upper limit of the resonance frequency at high temperature, \( E_a \) is the thermal activation energy, \( T_i \) is the freezing temperature of the dipoles and \( K \) is the Boltzmann constant. If we write \( \log f = X \) and \( \log f_0 = X_0 \), then Eq. (3) becomes

\[
X = X_0 - \frac{E_a}{K(T_m - T_i)} = X_0 + \frac{E_a}{K} \log f_0 - \frac{E_a}{K} \log f + \ldots \]

Hence, the ratio \( T_m(f)/T_m(1 \text{ kHz}) \) follows a linear variation on \( \log f \):

\[
T_m(f)/T_m(1 \text{ kHz}) = C + SL \log f,
\]

where \( C \) and \( SL \) are constant.

Fig. 11 shows the result of plotting \( T_m(f)/T_m(1 \text{ kHz}) \) versus \( \log f \) for CSNNT0.7 ceramic sample. As can be seen in this figure, the dependence on \( \log f \) for the composition 0.7 fit well with a linear relation. The value of 1 kHz as the reference frequency was selected as it is currently used in the international electronics standards. It is interesting that the plot of \( T_m(f)/T_m(1 \text{ kHz}) \) could represent a general and convenient method to compare various relaxor materials, the \( SL \) of the line is thus a constant for a given ceramic which gives a level of the relaxor effect.

The value of the slope of the straight lines gives the “degree” of the relaxor effect. All these observations strongly indicate that the compound for \( x=0.7 \) is a good relaxor ferroelectric. In order to demonstrate the ferroelectric character of the material, we attempt to measure the hysteresis of polarized ceramics at room temperature.

### 3.4. Ferroelectric hysteresis

In order to confirm the ferroelectric behavior of these compounds, we have chosen the composition \( x=0.9 \) as an example. The ferroelectric behavior was characterized using polarization versus electric field (\( P-E \)) hysteresis loops...
measured at room temperature. The typical polarization–electric field ($P-E$) hysteresis loops of CSNNT$_x$ with $x=0.9$ ceramic was shown in Fig. 12. Non-linear $P-E$ hysteresis loops are observed. The remanent polarization $P_r$ was found to be $0.038$ μC/m$^2$ with a coercive field $E_C$ of $3$ (V/mm). The shape of hysteresis loop clearly shows a typical ferroelectric phase and confirms the good densification of this ceramic.

4. Raman spectroscopy

For the Raman spectroscopic measurements, the scattered radiation was analyzed with a Ram HR triple monochromator. The spectra slit widths were set to maintain a resolution of approximately $3$ cm$^{-1}$. The excitation light was $514.5$ nm line of argon ion laser.

Raman scattering seems to be one of the appropriate techniques to study the dynamics of structure by analyzing the characteristic modes associated with nanoregions in relaxors.

Fig. 13 shows the Raman spectra of the relaxor CSNNT0.7 ceramic composition around the ferroelectric–paraelectric phase transition in the frequency range ($100$–$1600$ cm$^{-1}$) at room temperature. From this evolution, we observe four bands denoted by F1, F2, F3 and F4. These bands appear at frequencies not very different from those of NaNbO$_3$ [37]. In fact, the peak F2 attributed to the A1 (TO) phonon Raman spectrum observed at $276$ cm$^{-1}$ for NaNbO$_3$ associated with first order Raman spectrum is observed at $260$ cm$^{-1}$ in our material. This behavior means that the substitution of NaNbO$_3$ in the A and B sites of the perovskite structure introduces an important disorder in the structure. Thus, we favor the relaxor character in material. However, the peak F3 observed at $602$ cm$^{-1}$ for NaNbO$_3$ is observed in this composition at $590$ cm$^{-1}$. The sharp peaks observed at low frequency ($<70$ cm$^{-1}$) are due to the electronic of the Raman spectra apparatus.

5. Conclusion

The Ca$_{1-x}$Na$_x$ (Ti$_{0.9}$Sn$_{0.1}$)$_x$Nb$_3$O$_9$ solid solution was successfully synthesized by a solid-solution method and investigated by several physical methods. The X-ray diffraction analysis of CSNNTx, with $x=0.7$ and $x=0.8$, exhibits cubic and tetragonal phases, respectively. Regarding the dielectric measurements, they show two kinds of behavior depending on the composition: a ferroelectric classic for $x \geq 0.8$ and a relaxor behavior for $x < 0.8$. As for the polarization hysteresis measurements below this transition, they have confirmed the existence of the ferroelectric phase. The evolution of the Raman spectra for $x=0.7$ at room
temperatures confirms our structural and dielectric results. Some of these new compositions are of interest for application thanks to their physical properties and environmentally friendly character.

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