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Microstructure, X-ray diffraction, dielectric and Raman spectroscopy studies of $Ca_xSr_yBa_{1-(y+x)}Nb_2O_6$ ceramics

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ABSTRACT

We have studied $Ca_xSr_yBa_{1-(y+x)}Nb_2O_6$ (CSBN(x)) ceramics with tungsten-bronze structure. Ceramics were prepared with the conventional solid-state reaction for (x = 0.1, y = 0.1), (x = 0.1, y = 0.2) and (x = 0.2, y = 0.1). Phase purity, structure and crystallinity were investigated with X-ray diffraction showing pure phases with tetragonal symmetries. Microstructural analysis was performed using SEM. The microstructure of CSBN(x) ceramics showed a variation in grain shape and size. Dielectric measurements indicated the presence of ferroelectric-paraelectric phase transition at high temperatures which has been confirmed by DSC analyses. Polarizations versus electric field (P-E) loops were measured at different temperature. The Raman spectra of CSBN(x) as a function of temperature were also recorded in order to investigate the phase transformation. The vibrational spectra of CSBN(x) ceramics are dominated by broad and multi-component bands related to the internal vibrations of the NbO_6 octahedral.

1. Introduction

Crystals of ferroelectric niobates with the structure of tungsten bronze, such as strontium barium niobate $Sr_xBa_{1-x}Nb_2O_6$ (SBN) and calcium barium niobate $Ca_xBa_{1-x}Nb_2O_6$ (CBN) are the subject of intense investigations owing to their interesting dielectric, piezoelectric, pyroelectric and non linear electro-optical properties.

The ferroelectric material strontium-barium-niobate ($Sr_xBa_{1-x}Nb_2O_6$, SBN) exhibits a low phase transition temperature of about 353 K for the congruently melting composition with 61 mol% strontium content (SBN: 61) which hampers its applicability. But CBN has an about 200 K higher phase transition temperature for the congruently melting composition with 28 mole% of calcium (CBN:28) [1]. Previous studies demonstrated that CBN does not show a clear relaxor like behavior as SBN [2]. Hence it is anticipated that $Ca_xSr_yBa_{1-(y+x)}Nb_2O_6$ enables a suitable tuning of the physical properties and in particular obtaining the required value of the Curie temperature yet no relevant work has been reported. Moreover, results reported by Jing Zhang et al. [3] revealed that the transition temperatures (T_C) of $Ca_x(Sr_{0.5}Ba_{0.5})_{1-x}Nb_2O_6$ ceramics are all around 90 °C and revealed that the dielectric properties of SBN ceramics were enhanced by the Ca-dopant.

The tungsten bronze (TB) structure can be developed from the perovskite type structure by tilting the oxygen octahedral in the way to form a lattice with three different types of voids. TB structure has a chemical formula of $(A_1)_2(A_2)_4(C)_4(B)_{10}O_{30}$, the A_1, A_2, C, and B sites are the 12-, 15-, 9-, and 6-fold-coordinated oxygen octahedral sites, respectively, with the A sites occupied by Sr, Ba, Ca, Pb, K, or Na, the C sites by Li, and the B sites by either Nb or Ta. In the SCBN crystal, Sr^{+2} ions, Ca^{+2} ions and Ba^{+2} ions occupy the A sites, whereas Nb^{+5} ions occupy the B sites and form [NbO_6] octahedral with six oxygen atoms.

Recently, Phase diagram analyses and crystal growth experiments of the ferroelectric tetragonal tungsten $Ca_xSr_yBa_{1-x-y}Nb_2O_6$ (calcium strontium barium niobate, CSBN) were studied by Muehlberg et al. [4].

The aim of this work is to study the crystal structure of the $Ca_xSr_yBa_{1-(y+x)}Nb_2O_6$ (SCBN) compounds where x = 0.1, 0.1, 0.2 and the corresponding y = 0.1, 0.2 and 0.1, respectively. The evolution of the Raman spectra was also studied as a function of various compositions at different temperatures. DSC measurements have been done in all of our samples. Also dielectric and ferroelectric properties have been investigated.

2. Experimental procedure

The $Ca_xSr_yBa_{1-(y+x)}Nb_2O_6$ (CSBN(x)) for (x = 0.1, y = 0.1),

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($x = 0.1, y = 0.2$) and ($x = 0.2, y = 0.1$) ceramics were prepared by a conventional solid-state method. Stoichiometric amounts of high purity (up 99%) $BaCO_3$, $CaCO_3$, $SrCO_3$ and Nb_2O_5) powders were used. In order to eliminate H_2O: $BaCO_3$, $CaCO_3$, $SrCO_3$ and Nb_2O_5 were preheated at 200 °C for 4 h before use. The appropriate mixtures of powders were calcined at 1100 °C for 5 h under oxygen atmosphere and cooled to room temperature. After calcination, powders were mixed for 2 h and pressed under 100 MPa into 8 mm diameter and about 1 mm thick. Finally, the pellets were sintered in oxygen atmosphere at 1350 °C for 4 h followed by natural cooling. The compactness value, C (defined as the ratio between the experimental density d_{exp}, and theoretical density d_{theor}) obtained for sintered samples were in the range 92–95%.

Room temperature powder X-ray diffraction patterns were realized using a Philips diffractometer using $CuK_{\alpha 1}$ radiation ($\lambda = 1.5406$ Å) in the angle range $20° \leq 2\theta \leq 100°$ with 10 s counting time for each step of 0.02° in order to determine the structure for all prepared ceramic compositions.

The dielectric measurements were performed on ceramic discs after deposition of gold electrodes on the circular faces by cathodic sputtering. The dielectric measurements were studied using LCR meter HP 4284A. The temperature and frequency ranges were in the range of 300–700 K and 1–1000 KHz, respectively.

Differential scanning calorimetry (DSC) analyses were carried out under nitrogen gas with a heating rate of 10 °C/min using 20 mg of crushed ceramics in crimped aluminum pans. Microstructural analysis was realized using SEM. The Polarization-Electric field (P–E) hysteresis measurements were recorded at room temperature using an automatic PE loop tracer based on Sawyer–Tower circuit [5].

Raman spectra of sintered samples are recorded from 50 to 1000 cm^{-1} in a micro-Raman Spectrometer (LABRAM HR- 800), working in a backscattering configuration, equipped with an He^+ ion ($\lambda = 633$ nm) laser. The spectral resolution of the system is 3 cm^{-1}.

3. Results and discussion

3.1. Microstructures

Fig. 1 shows the SEM micrographs of the $Ca_xSr_yBa_{1-(y+x)}Nb_2O_6$ (CSBN(x)) ceramics with different x sintered at the same temperature of 1350 °C. It was clearly seen from the figure that the concentration of Ca or Sr influences on the average grain size and homogeneity of the grains.

In CSBN(x) (($x = 0.1, y = 0.2$) and ($x = 0.2, y = 0.1$)), the duplex microstructure consists of a large number of very small grains of size, and they are sandwiched between very large grains of size. The microcracks are due to internal strains resulting from the abnormal grain growth.

The origin of such abnormal grain growth as well as duplex microstructure has not been clearly understood. A number of possible explanations have been offered in the literature for the occurrence of abnormal grain growth. Takahashi et al. [6] have reported that the abnormal grain growth is due to the liquid phase resulting from local inhomogeneous composition due to partial incompletion of calcination. Fang et al. [7] have suggested that it is due to formation of $SrNb_2O_6$, a low-melting second phase, at the grain boundary. This has been attributed to the decomposition of stoichiometric SBN during ball milling. Lee and Freer [8] and Kim et al. [9] have reported that the formation of Nb-rich/Ba-poor phase at the grain boundary is the cause of the formation of low-melting liquid phase, which in turn results in the formation of the abnormal grain growth.

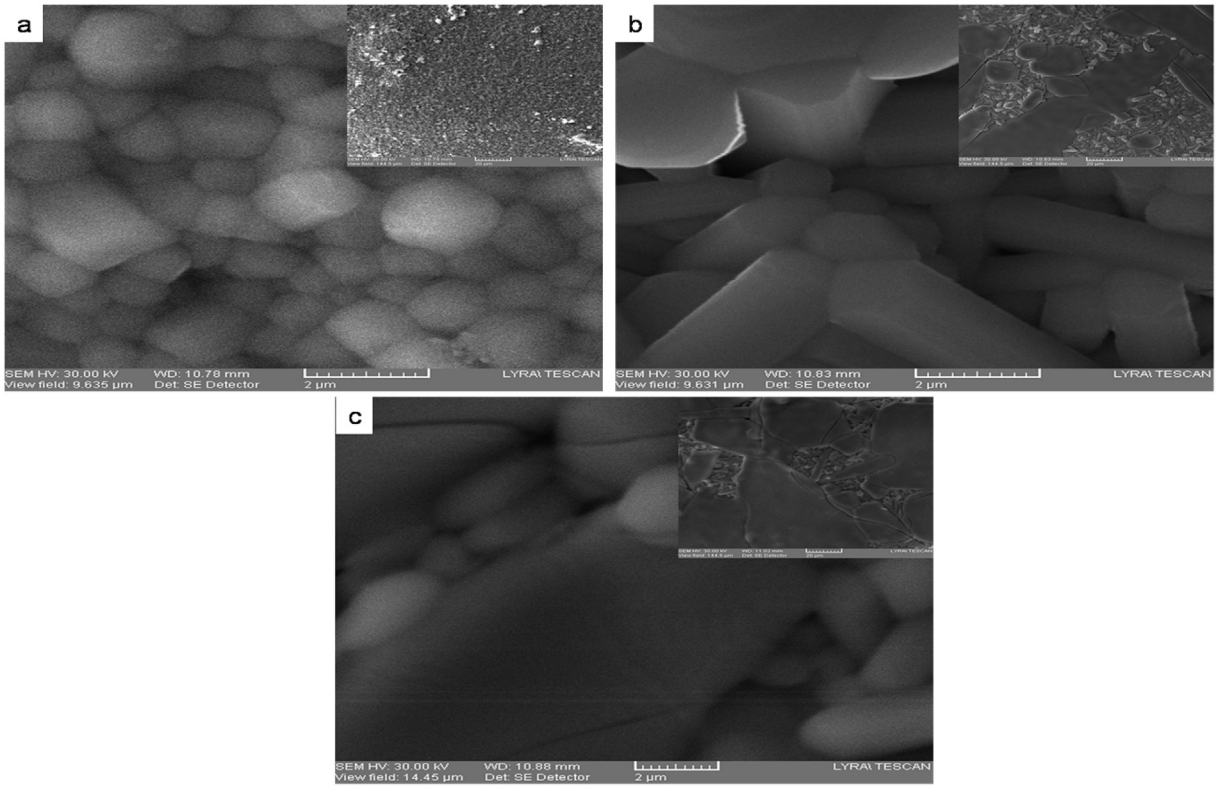

Fig. 1. Microstructure of the $Ca_xSr_yBa_{1-(y+x)}Nb_2O_6$: (a) ($x = 0.1, y = 0.1$), (b) ($x = 0.1, y = 0.2$), (c) ($x = 0.2, y = 0.1$) compounds.