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Journal of Alloys and Compounds 429 (2007) 280–284

Journal of ALLOYS AND COMPOUNDS

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High permittivity and low loss dielectric ceramics $Ba_5LnNiNb_9O_{30}$ (Ln = La, Nd and Sm)

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Received 16 December 2005; received in revised form 22 February 2006; accepted 4 April 2006
Available online 5 May 2006

Abstract

Three novel $Ba_5LnNiNb_9O_{30}$ (Ln = La, Nd and Sm) ceramics were prepared and characterized in the $BaO–Ln_2O_3–NiO–Nb_2O_5$ system. All three compounds are paraelectric phases adopting the filled tetragonal tungsten bronze (TB) structure at room temperature. At 1 MHz, $Ba_5LnNiNb_9O_{30}$ ceramics have a high dielectric constants in the range 193–245.3, a low dielectric loss in range 0.0059–0.0087, and the temperature coefficients of the dielectric constant (τ_ε) in the range −1140 to −1310 ppm °C^{-1}.

Keywords: Ceramics; Solid state reaction; Microstructure; X-ray diffraction

1. Introduction

Tungsten–bronze (TB) compounds belong to an important family of dielectric materials, which display interesting ferroelectric, pyroelectric, piezoelectric, and nonlinear optic behaviors [1–6]. In previous investigations, the ferroelectric nature of TB compounds has been especially emphasized, but less attention has been focused on those compounds with paraelectric nature, which occur in the TB family. Recently, in order to pursue high dielectric constant ceramics for applications in microwave telecommunication, discrete and multilayer (MLC) capacitors. Sebastian et al. proposed some promising compounds with tungsten bronze (TB) structure under the formula Ba_3 (Re)$_3Ti_5Nb_5O_{30}$ (Re = La, Y, Sm and Nd) for the dielectric constant above 130 [6–11]. Chen et al. also reported the presence of dielectric materials with filled TB structure with high dielectric constant and low dielectric loss in the $BaO–Ln_2O_3–TiO_3–Ta_2O_5$ system (Ln = La, Sm and Nd) [7–10]. Those materials such as $Ba_5SmTi_3Ta_7O_{30}$ and $Ba_5LaTi_3Ta_7O_{30}$ have dielectric constant in the range of 70–175 and low dielectric loss of the order of 10^{-3}, but the problem for the above systems is the relatively large negative temperature coefficient of dielectric constant ($\tau_\varepsilon \sim -1500$ ppm °C^{-1}).

The TB structure consists of a complex array of distorted BO_6 octahedra sharing corners in such a way that three different types of interstices (A, B and C) are available for a wide variety of cations occupying in the general formula $(A_1)_2(A_2)_4(C)_4(B_1)_2(B_2)_8O_{30}$. It has been found that different ionic substitutions at above-mentioned sites can play an important role in tailoring their physical properties [11,12]. Therefore, we conducted the systematic studies on the characterization and dielectric properties of Sr-based TB ceramics $Sr_5LnTi_3Ta_7O_{30}$ and $Sr_4Ln_2Ti_4Ta_6O_{30}$, Sn-contained ceramics $A_5LnSn_3Nb_7O_{30}$ (A = Ba and Sr), and Zn-contained TB ceramics $Ba_5LnZnM_9O_{30}$ (M = Ta and Nb) [12–21]. Since very little data are available on Ni-contained TB compounds, this paper firstly presents the preparation, characterization and dielectric properties of new TB compounds $Ba_5LnNiNb_9O_{30}$ (Ln = La, Nd and Sm).

2. Experimental

Stoichiometric amounts of high purity powders of $BaCO_3$ (>99.5%), Ln_2O_3 (Ln = La, Nd and Sm) (>99.5%), Ni_2O_3 (>99.95%) and Nb_2O_5 (>99.9%) were weighed and fully mixed through ball milling with zirconia media in ethanol for 24 h. The mixtures were dried and calcined in the temperature range 1350–1380 °C for 6 h. The calcined powders were thoroughly reground and mixed with a 5% solution of polyvinyl alcohol (PVA) as a binder. The slurries

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doi:10.1016/j.jallcom.2006.04.002

were then dried, ground and pressed into cylindrical compacts of different thickness in the range 2–4 and 11 mm in diameter under a pressure of 150 MPa. The green compacts were initially fired at a rate of 3 °C/min up to 600 °C and then at a rate of 12 °C/min to the sintering temperature. An intermediate soaking at 600 °C for 2 h was allowed to expel the binder. The optimized sintering temperatures were 1340 °C for $Ba_5LaNiNb_9O_{30}$ (BLNN), 1360 °C for $Ba_5NdNiNb_9O_{30}$ (BNNN), and 1380 °C for $Ba_5SmNiNb_9O_{30}$ (BSNN). The sintering was carried out for a duration of 4 h in air. The densities of the compacts were measured by the Archimedes method. The phase constitutions of the samples were examined using a Rigaku D/MAX-RB X-ray diffractometer (XRD) using Cu Kα radiation ($\lambda = 0.15406$ nm). The microstructures were studied using a JSM-5610LV scanning electron microscopy (SEM).

Silver paste was applied to the circular faces, then dried at 600 °C for 20 min and cooled naturally to room temperature. Temperature-dependent dielectric measurements were made using an HP4284A LCR meter equipped with a thermostat from room temperature (20 °C) to 150 °C at 1, 10, 100 kHz and 1 MHz. The temperature coefficient of the dielectric constant (τ_ε) were calculated using the data in the temperature range of 20–80 °C at 1 MHz.

3. Results and discussion

The XRD patterns obtained for the ceramics using Cu Kα radiation are shown in Fig. 1. The patterns are similar to the one reported for tetragonal tungsten bronze (TTB) compound $Ba_6Ni_{0.67}Ta_{9.33}O_{30}$ by Fang et al. (JCPDS file No. 54-1164) [21]. All peaks were indexed, and there was no evidence for any second phase(s) present such that these ceramics are single-phase pure. The unit cell parameters of the three compounds refined by the least-squares method are listed in Table 1. With the radius of Ln^{3+} increasing, the unit cell parameters of $Ba_5LnNiNb_9O_{30}$ also slightly increase. Since the TB structure is based on five crystallographic sites, it is difficult to precisely

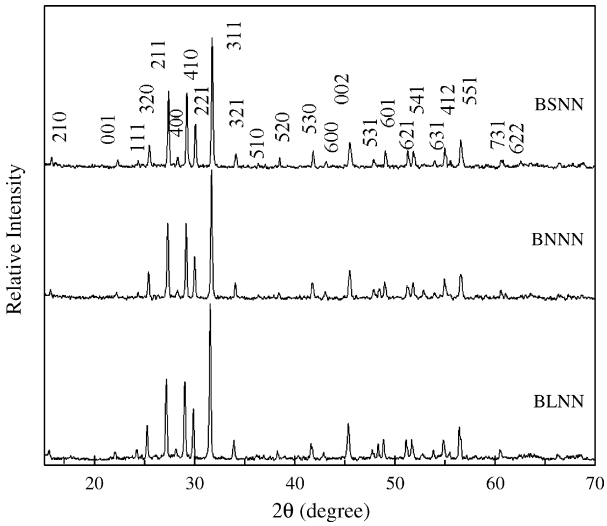

Fig. 1. X-ray powder diffraction patterns of $Ba_5LnNiNb_9O_{30}$.

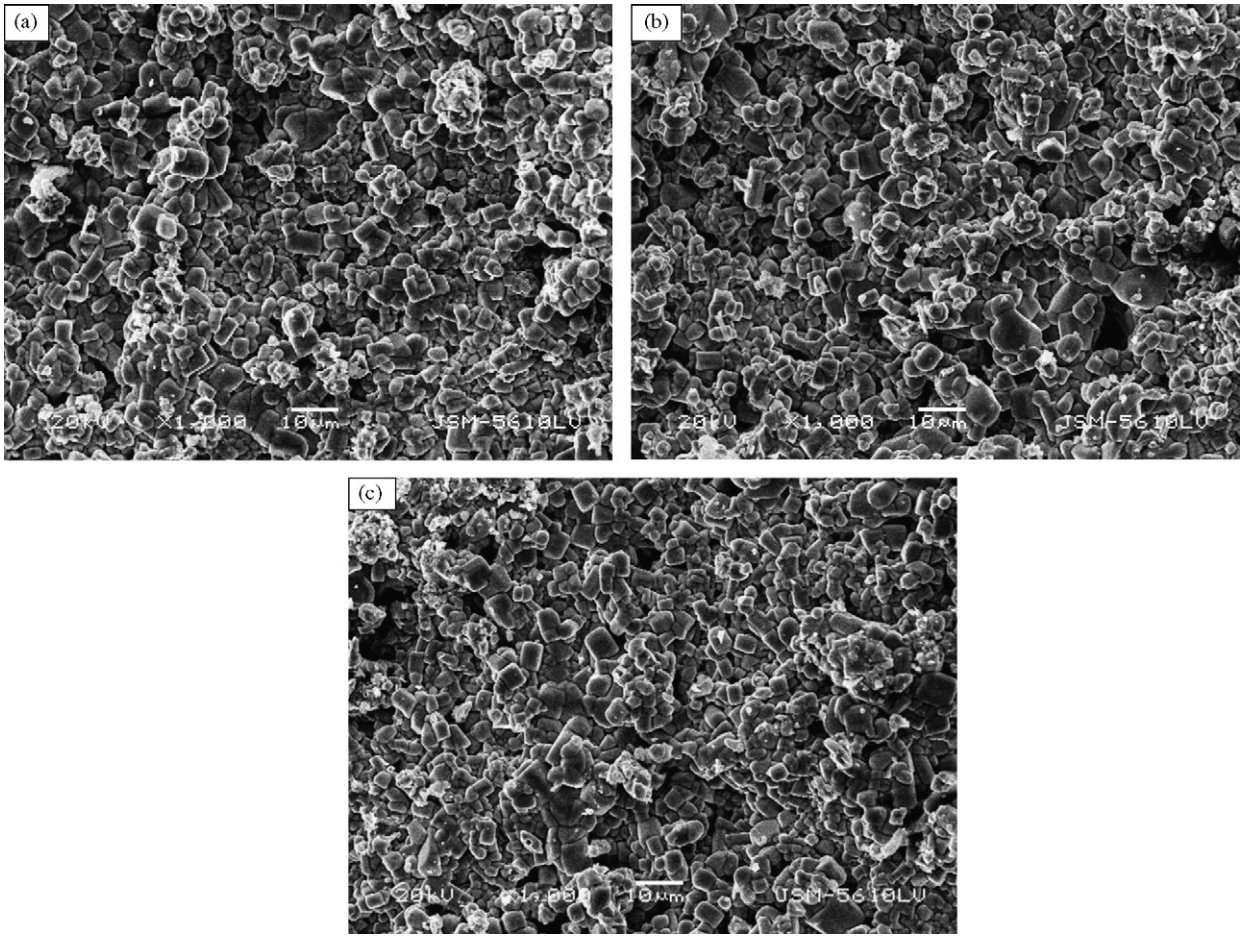

Fig. 2. SEM micrographs of the fracture surfaces of (a) BLNN, (b) BNNN, and (c) BSNN ceramics.