Characterization and dielectric properties of Ba$_5$LnNiTa$_9$O$_{30}$ (Ln = La, Nd and Sm) ceramics

L. Fang · H. Zhang · T. H. Huang · F. C. Meng · J. F. Yang

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Abstract Three novel Ba$_5$LnNiTa$_9$O$_{30}$ (Ln = La, Nd and Sm) ceramics were prepared and characterized in the BaO-Ln$_2$O$_3$-NiO-Ta$_2$O$_5$ system. All three compounds adopted the filled tetragonal tungsten bronze (TB) structure at room temperature. The present ceramics exhibited relaxor behavior, and the Curie temperature (at 10kHz) were $-130$, $-80$ and $-45$ °C for Ba$_5$LaNiTa$_9$O$_{30}$, Ba$_5$NdNiTa$_9$O$_{30}$, and Ba$_5$SmNiTa$_9$O$_{30}$ respectively. At room temperature, Ba$_5$LnNiTa$_9$O$_{30}$ ceramics have a high dielectric constants in the range 102~118, a low dielectric loss in range 0.0019~0.0036, and the temperature coefficients of the dielectric constant ($\tau_\varepsilon$) in the range $-320$~$-460$ ppm/°C (at 1 MHz).

Keywords Tungsten bronze structure · Dielectric properties · Ba$_5$LnNiTa$_9$O$_{30}$ · X-ray diffraction

1. Introduction

Recently, some ferroelectric niobates and tantalites with tungsten-bronze (TB) structure have attracted much attention due to their interesting ferroelectric, pyroelectric, piezoelectric, and nonlinear optic properties for applications in various electric devices, such as transducers, actuators, capacitors, and ferroelectric random access memory [1–6]. Some paraelectric niobates and with high dielectric constant and low loss are also very important due to the rapid progress in microwave telecommunications, satellite broadcasting and other related devices [7–9]. 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$_2$)$_8$O$_{30}$ [1–3]. Generally, the smallest interstice C is empty, so the general formula is A$_6$B$_{10}$O$_{30}$ for the filled tungsten–bronze structure. It has been found that different ionic substitutions at abovementioned sites can play an important role in tailoring their physical properties.

In order to find some new filled tungsten–bronze ceramics, some works have been carried out in quaternary systems containing rare earths [6–11]. Sebastian and Chen et al. proposed some promising candidates for high dielectric constant ($\varepsilon > 100$) dielectric ceramics with filled tungsten–bronze structure in BaO-Ln$_2$O$_3$-TiO$_2$-M$_2$O$_5$ system (Ln = La, Sm, Nd; M = Ta, Nb) [7–10]. We recently conducted the systematic studies on the preparation and dielectric properties of Sr-based TB ceramics such as Sr$_5$LnTi$_3$Ta$_7$O$_{30}$ and Sr$_4$Ln$_2$Ti$_4$Ta$_6$O$_{30}$ [12–15], Sn-contained ceramics A$_3$LnSn$_3$Nb$_2$O$_{30}$ (A = Ba, Sr) [16, 17], and Zn-contained TB ceramics Ba$_5$LnZnM$_9$O$_{30}$ (M = Ta, Nb) [18–20]. Since very little data are available on TB compounds in the BaO-Ln$_2$O$_3$-NiO-Ta$_2$O$_5$ system, this paper firstly presents the preparation, characterization and dielectric properties of new TB compounds Ba$_5$LnNiTa$_9$O$_{30}$ (Ln = La, Nd, Sm). Meanwhile, the effect of different Ln ions in A sites on dielectric properties and crystal structure were also discussed.

2. Experimental

Stoichiometric amounts of high purity powders of BaCO$_3$ (>99.5%), Ln$_2$O$_3$ (Ln = La, Nd, Sm) (>99.5%), Ni$_2$O$_3$ (>99.95%) and Ta$_2$O$_5$ (>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 were then dried, ground and pressed into cylindrical compacts of different thickness in the range 2–4 mm 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 1400°C for Ba5LaNiTa9O30 (BLNT), 1420°C for Ba5NdNiTa9O30 (BNNT), and 1440°C for Ba5SmNiTa9O30 (BSNT). 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 CuKα radiation (λ = 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 minutes and cooled naturally to room temperature. Temperature-dependent dielectric measurements were made using an HP4284A LCR meter from −170°C to 400°C at 10, 100 kHz and 1 MHz. The temperature coefficient of the dielectric constant (τe) 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 CuKα radiation are shown in Fig. 1. The patterns are similar and match with the one reported for tetragonal tungsten bronzes (TTB) compound Ba6Ni0.67Ta9.33O30 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 Ln3+ increasing, the unit cell parameters of Ba5LnNiTa9O30 also slightly increase. Since the TB structure is based on five crystallographic sites, it is difficult to precisely determine the coordination of those ions based on the current results. However, the course of the ionic radii suggests that Ba2+ predominantly occupies the 15-fold coordinated A2 sites, and Ta5+ and Ni2+ occupy the 6-fold coordinated B sites.

Ferroelectric tungsten–bronze compounds usually can be divided into two groups: those with tetragonal symmetry (4 mm), which undergo only one phase transition corresponding to tetragonal ferroelectric (4 mm) to tetragonal paraelectric (4/mmm), and those with orthorhombic symmetry (mm2) which are both and ferroelastic, and undergo two phase transitions corresponding to orthorhombic ferroelectric (mm2) to tetragonal ferroelectric (4 mm) and from ferroelectric to paraelectric [2, 3]. Since the distortion from tetragonal symmetry (4 mm) to orthorhombic symmetry (mm2) is very weak, it is difficult to determine the symmetry of tungsten–bronze compounds by the X-ray powder diffraction and often requires other techniques such as ferroelectric, dielectric or optical measurements [2, 3, 10]. In this study Ba5LnNiTa9O30 is found to be tetragonal tungsten–bronze structure (TTB) by latter dielectric measurements.

Since Ba5LnNiTa9O30 adopt the TTB structure at room temperature, then the stability of their TB structure can be evaluated by the tolerance factor proposed by Wakiya et al. [4]. According to the general formula, there are two kinds of A sites for TTB structure; one is the A1 site with 12-fold coordination which is identical to that in perovskite structure, and the other is the A2 site with 15-fold coordination. Therefore two kinds of tolerance factors for A sites can be given by the following equations:

\[
t_{A1} = \frac{r_{A1} + r_O}{\sqrt{2}(r_B + r_O)}
\]

Table 1 The unit cell parameters, tolerance factor and electronegativity differences of Ba5LnNiTa9O30

<table>
<thead>
<tr>
<th>Compounds</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>V (Å³)</th>
<th>Tolerance factor</th>
<th>Electronegativity difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>BLNT</td>
<td>12.5673(3)</td>
<td>3.9550(2)</td>
<td>624.64</td>
<td>0.992</td>
<td>2.194</td>
</tr>
<tr>
<td>BNNT</td>
<td>12.5537(3)</td>
<td>3.9475(2)</td>
<td>622.11</td>
<td>0.987</td>
<td>2.188</td>
</tr>
<tr>
<td>BSNT</td>
<td>12.5424(3)</td>
<td>3.9409(2)</td>
<td>619.94</td>
<td>0.985</td>
<td>2.188</td>
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