

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

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

Received: 16 May 2004 / Revised: 20 April 2005 / Accepted: 17 August 2005
© Springer Science + Business Media, Inc. 2006

Abstract Three novel $\text{Ba}_5\text{LnNiTa}_9\text{O}_{30}$ (Ln = La, Nd and Sm) ceramics were prepared and characterized in the $\text{BaO-Ln}_2\text{O}_3\text{-NiO-Ta}_2\text{O}_5$ 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 $\text{Ba}_5\text{LaNiTa}_9\text{O}_{30}$, $\text{Ba}_5\text{NdNiTa}_9\text{O}_{30}$, and $\text{Ba}_5\text{SmNiTa}_9\text{O}_{30}$ respectively. At room temperature, $\text{Ba}_5\text{LnNiTa}_9\text{O}_{30}$ 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 (τ_ϵ) in the range $-320\sim-460\text{ ppm }^\circ\text{C}^{-1}$ (at 1 MHz).

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

1. Introduction

Recently, some ferroelectric niobates and tantalates 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 $(\text{A}_1)_2(\text{A}_2)_4(\text{C})_4(\text{B}_1)_2(\text{B}_2)_8\text{O}_{30}$ [1–3]. Generally, the smallest interstice C is empty, so the general formula is $\text{A}_6\text{B}_{10}\text{O}_{30}$ for the filled tungsten-bronze structure. It has been found that different ionic substitutions at above-mentioned 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 ($\epsilon > 100$) dielectric ceramics with filled tungsten-bronze structure in $\text{BaO-Ln}_2\text{O}_3\text{-TiO}_3\text{-M}_2\text{O}_5$ 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 $\text{Sr}_5\text{LnTi}_3\text{Ta}_7\text{O}_{30}$ and $\text{Sr}_4\text{Ln}_2\text{Ti}_4\text{Ta}_6\text{O}_{30}$ [12–15], Sn-contained ceramics $\text{A}_5\text{LnSn}_3\text{Nb}_7\text{O}_{30}$ (A = Ba, Sr) [16, 17], and Zn-contained TB ceramics $\text{Ba}_5\text{LnZnM}_9\text{O}_{30}$ (M = Ta, Nb) [18–20]. Since very little data are available on TB compounds in the $\text{BaO-Ln}_2\text{O}_3\text{-NiO-Ta}_2\text{O}_5$ system, this paper firstly presents the preparation, characterization and dielectric properties of new TB compounds $\text{Ba}_5\text{LnNiTa}_9\text{O}_{30}$ (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_2O_3 (Ln = La, Nd, Sm) (>99.5%), Ni_2O_3 (>99.95%) and Ta_2O_5 (>99.9%) were weighed and fully

L. Fang (✉) · H. Zhang · T. H. Huang · F. C. Meng · J. F. Yang
State Key Lab. of Advanced Technology for Materials Synthesis
and Processing, Wuhan University of Technology, Wuhan
430070, People's Republic of China
email: fangliang001@263.net

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 CuK α 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 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 (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 CuK α radiation are shown in Fig. 1. The patterns are similar and match with the one reported for reported for tetragonal tungsten bronze (TTB) compound Ba₆Ni_{0.67}Ta_{9.33}O₃₀ 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. How-

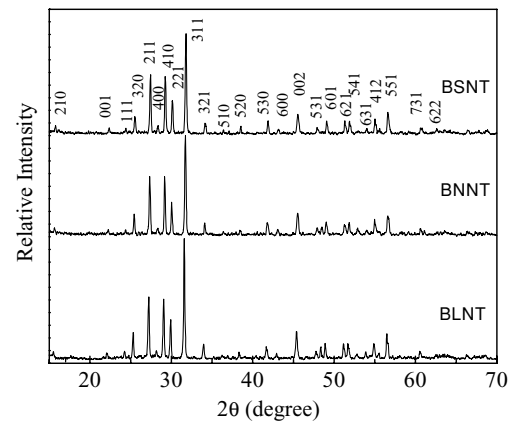


Fig. 1 X-ray powder diffraction patterns of Ba₅LnNiTa₉O₃₀

ever, 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 ferroelastic, and undergo two phase transitions corresponding to orthorhombic ferroelastic (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:

$$t_{A1} = \frac{r_{A1} + r_O}{\sqrt{2}(r_B + r_O)} \quad (1)$$

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

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

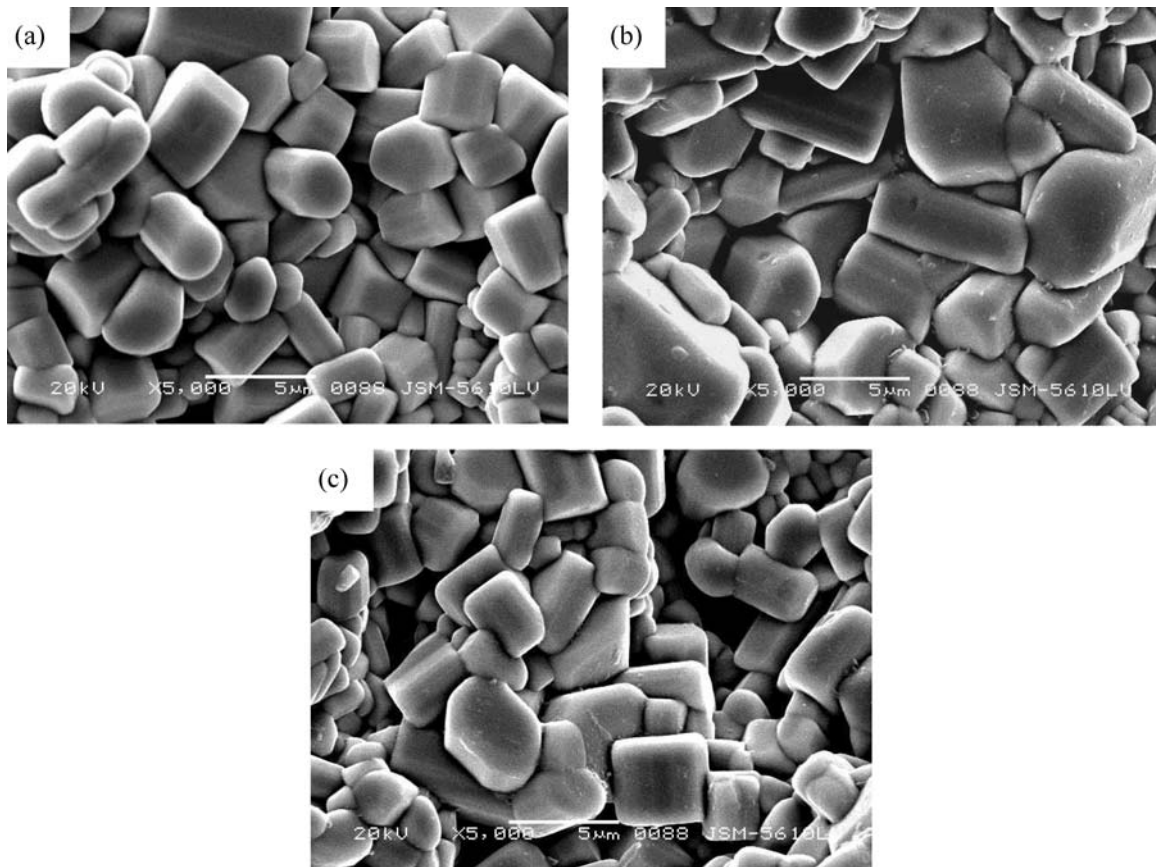


Fig. 2 SEM micrographs of the fracture surfaces of (a) BLNT, (b) BNNT, and (c) BSNT ceramics

$$t_{A2} = \frac{r_{A2} + r_O}{\sqrt{23 - 12\sqrt{3}}(r_B + r_O)} \tag{2}$$

where r_A , r_B and r_O are the ionic radii of the A and B site ions and O^{2-} , respectively. In order to better understand the relationship between tolerance factor and the stability of TTB structure, an averaged tolerance factor can be denoted as:

$$t = \frac{t_{A1} + 2t_{A2}}{3} \tag{3}$$

One the other hand, the averaged electronegativity difference is another important parameter to evaluate the stability of the crystal structure written as:

$$e = \frac{(\chi_A - \chi_O) + (\chi_B - \chi_O)}{2} \tag{4}$$

where χ_A, χ_B and χ_O are the individual electronegativities of the A, B site cations and O^{2-} , respectively. By using the general formula for the present tungsten bronze compounds of $Ba_5LnNiTa_9O_{30}$ ($Ln = La, Nd$ and Sm), the averaged

electronegativity difference e can be written as:

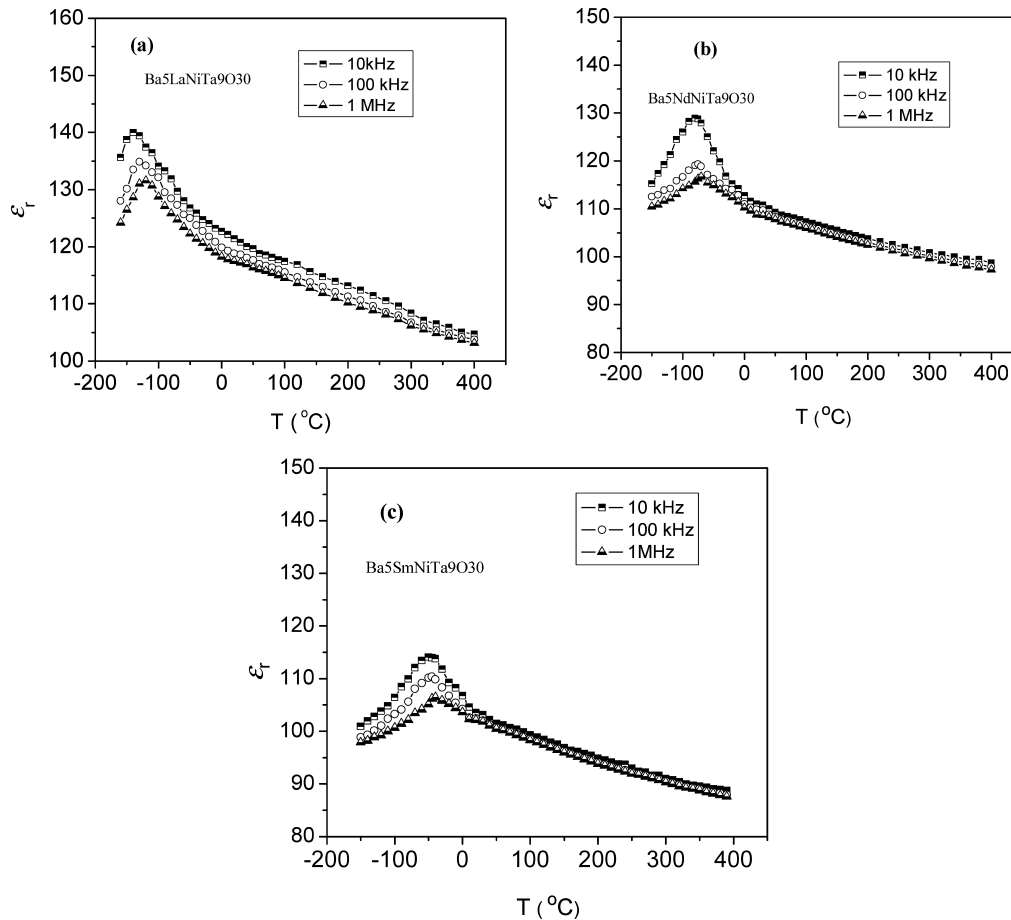
$$e = \frac{5(\chi_{Ba} - \chi_O) + (\chi_{Ln} - \chi_O) + (\chi_{Ni} - \chi_O) + 9(\chi_{Ta} - \chi_O)}{16} \tag{5}$$

As shown in Table 1, the averaged tolerance factors and electronegativity differences of $Ba_5LnNiTa_9O_{30}$ have been calculated using the revised effective ionic radii [22] and Pauling’s electronegativity [23]. With the radius of Ln^{3+} increasing, the tolerance factor increases from 0.985 to 0.992, and the electronegativity difference increases from 2.188 to 2.194, which are higher than the values of $Ba_4Sm_2Ti_4Ta_6O_{30}$ (0.97 and 2.12) reported by Chen et al. as the low limit for the stabilization of the TB structure [9–10]. Therefore, $Ba_5LnNiTa_9O_{30}$ adopt the stable TB structure without any secondary phase.

The new compounds were sintered into dense ceramics without the use of any additive. They show a bulk density of 7.606 gcm^{-3} (95.2%), 7.697 gcm^{-3} (96.3%), and 7.685 gcm^{-3} (95.5%) for BLNT, BNNT, and BSNT, respectively. Figure 2 gives the SEM micrographs of the fracture surfaces of the BLNT, BNNT and BSNT ceramics, respectively. These ceramics have a close microstructure with low porosity. The uniformly packed grains are in the size range of 2–8 μm .

Table 2 Room temperature dielectric properties of $\text{Ba}_5\text{LnNiTa}_9\text{O}_{30}$ ceramics

Composition	Sintering temperature	100 kHz		400 kHz		1 MHz	
		ϵ_r	$\tan \delta$	ϵ_r	$\tan \delta$	ϵ_r	$\tan \delta$
BLNT	1400	118.8	0.0017	118.4	0.0025	117.8	0.0036
BNNT	1420	109.9	0.0009	109.1	0.0012	108.74	0.0019
BSNT	1440	102.6	0.0013	102.5	0.0019	102.3	0.0027

**Fig. 3** Variation of the dielectric constant with temperature of $\text{Ba}_5\text{LnNiTa}_9\text{O}_{30}$ ceramics

The room-temperature (20°C) dielectric characteristics of the $\text{Ba}_5\text{LnNiTa}_9\text{O}_{30}$ ceramics are shown in Table 2. The dielectric constant is almost frequency independent, while the dielectric loss slightly increases with increasing frequency. These ceramics have high dielectric constants ϵ_r of 102–118 and low dielectric loss ($\tan\delta$) of 0.0019–0.0036 at 1 MHz. The dielectric constant of $\text{Ba}_5\text{LnNiTa}_9\text{O}_{30}$ are higher than those of $\text{Ba}_5\text{LnZnTa}_9\text{O}_{30}$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Sm}$) in the range 74–89 [18, 19]. The highest and the lowest dielectric constant are exhibited in BLNT and BSNT, respectively, similar to that shown in $\text{Ba}_5\text{LnZnTa}_9\text{O}_{30}$ ceramics.

The temperature dependency of the dielectric constants at 10 kHz, 100 kHz and 1 MHz are shown in Fig. 3. Dielectric constant increases with decreasing frequency due to the presence of all different types of polarization (electronic,

ionic, dipole and space charge) at low frequency. As temperature increases, there was only a significant peak of dielectric constant determined at -140°C , -80°C and -45°C (at 10 kHz) for BLNT, BNNT and BSNT, which suggest only one phase transition corresponding to ferroelectric-paraelectric phase transition from tetragonal $4mm$ symmetry to $4/mmm$ symmetry and confirm that three compounds adopt tetragonal TB structure and are paraelectric phase at room temperature [10, 11]. The temperature corresponding to the peaks is Curie temperature (T_C). The T_C is found to shift towards higher temperature side at higher frequencies, and this is the characteristic of relaxor ferroelectrics with TB structure [6, 10, 15]. The broadening of the dielectric peaks for the present ceramics may be attributed to the disorder distribution of cations at the A and B sites in TB

structure. The degree of disorderness or diffusivity (γ) can be calculated using the equation [24] $\ln(1/\varepsilon - 1/\varepsilon_{max}) = \gamma \ln(T - T_C) + \text{constant}$. The diffusivities γ calculated at 10 KHz for BLNT, BNNT and BSNT are 1.25, 1.31 and 1.39, respectively. γ is between 1 and 2 for three compounds, which confirms the diffused phase transition. The T_C of $\text{Ba}_5\text{LnNiTa}_9\text{O}_{30}$ decreased with increasing ionic radius from Sm^{3+} to La^{3+} , which agreed with the results reported by Choudhary and Chen et al in $\text{Sr}_5\text{LnTi}_3\text{Nb}_7\text{O}_{30}$ and $\text{Ba}_5\text{LnTi}_3\text{Nb}_7\text{O}_{30}$ ($\text{Ln}=\text{La}, \text{Nd}$ and Sm) [10, 24]. The temperature coefficients of dielectric constants are $-345 \text{ ppm}^\circ\text{C}^{-1}$ for BLNT, $-320 \text{ ppm}^\circ\text{C}^{-1}$ for BNNT, and $-460 \text{ ppm}^\circ\text{C}^{-1}$ for BSNT, which are slightly reduced compared to those of $\text{Ba}_5\text{LnZnTa}_9\text{O}_{30}$ in the range $-811 \sim -415 \text{ ppm}^\circ\text{C}^{-1}$ [18, 19] but are significantly reduced compared with those of the TB ceramics $\text{Ba}_5\text{LnTi}_3\text{Ta}_7\text{O}_{30}$ ($\text{Ln}=\text{La}, \text{Nd}, \text{Sm}$) in the range $-1347 \sim -2500 \text{ ppm}^\circ\text{C}^{-1}$ [9].

4. Conclusions

Three novel $\text{Ba}_5\text{LnNiTa}_9\text{O}_{30}$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Sm}$) ceramics in the $\text{BaO-Ln}_2\text{O}_3\text{-NiO-Nb}_2\text{O}_5$ quaternary system were prepared and characterized. BLZN, BNZN and BSZN adopt the filled tetragonal TB structure. These compounds exhibit significant relaxor behaviors, and the curie temperatures (at 10 kHz) are -140 , -80 and -45°C , respectively. At room temperature and at 1 MHz they have high dielectric constant and low dielectric loss, which is 117.8 and 0.0036 for $\text{Ba}_5\text{LaNiTa}_9\text{O}_{30}$, 108.7 and 0.0019 for $\text{Ba}_5\text{NdNiTa}_9\text{O}_{30}$, and 102.3 and 0.0027 for $\text{Ba}_5\text{SmNiTa}_9\text{O}_{30}$. In comparison with the TB ceramics $\text{Ba}_5\text{LnZnTa}_9\text{O}_{30}$ in the $\text{BaO-Ln}_2\text{O}_3\text{-ZnO-Ta}_2\text{O}_5$ system, the dielectric constants are significantly larger and the temperature coefficients of the dielectric constants (τ_ε) are reduced. These materials might have potential application as temperature-compensating dielectrics at room temperature and novel lead-free ferroelectrics at low temperature.

Acknowledgments This work was financially supported by Natural Science Foundation of China (NSFC No. 50572078 and 20571059) and the Major Program of MOE of China(No.0201). Mrs. Hui Zhang is thankful to DAAD for the scholarship.

References

1. R.R. Neurgaonkar and W.K. Cory, *J. Opt. Soc. Am. B*, **3**, 274 (1986).
2. R.R. Neurgaonkar, J.G. Nelson, J.R. Oliver, L.E. Cross, and W.K. Cory, *Mater. Res. Bull.*, **25**, 959 (1990).
3. R.R. Neurgaonkar, J.G. Nelson, and J.R. Oliver, *Mater. Res. Bull.*, **27**, 677 (1992).
4. N. Wakiya, J.K. Wang, A. Saiki, K. Shinozaki, and N. Mizutani, *J. Eur. Ceram. Soc.*, **19**, 1071 (1999).
5. L. Fang, H. Zhang, B.L. Wu, and R.Z. Yuan, *J. Progress in Crystal Growth and Characterization of Materials*, **40**, 161 (2000).
6. A. Panigrahi and N.K. Singh, *J. Mat. Sci. Lett.*, **18**, (1999) 1579.
7. P. Koshy, L.P. Kumari, and M.T. Sebastian, *J. Mat. Sci: Mater. Electron.*, **9**, 43 (1998).
8. R.P. Rao, S.K. Ghosh, and P. Koshy, *J. Mat. Sci: Mater. Electron.*, **12**, 729 (2001).
9. X.M. Chen, Y.H. Sun, and X.H. Zheng, *J. Eur. Ceram. Soc.*, **23**, 1571 (2003).
10. X.H. Zheng and X.M. Chen, *Solid State Communications*, **125**, 449 (2003).
11. L. Fang, H. Zhang, J.B. Yan, and W.M. Yang, *Acta Phys.-Chim. Sin.*, **19**, 82 (2003).
12. H. Zhang, L. Fang, T.H. Huang, H.X. Liu, R.Z. Yuan, and R. Dronskowski, *J. Mat. Sci.*, **40**, 529 (2005).
13. L. Fang, H. Zhang, R.Z. Yuan, and R. Dronskowski, *J. Mat. Sci: Mater. Electron.*, **15**, 699 (2004).
14. Liang Fang, H. Zhang, J.F. Yang, F.H. Meng, and R.Z. Yuan, *Mater. Lett.*, **58**, 1777 (2004).
15. L. Fang, H. Zhang, J.F. Yang, X.K. Hong, and F.C. Meng, *J. Mat. Sci: Mater. Electron.*, **15**, 355 (2004).
16. L. Fang, L. Chen, H. Zhang, C.L. Diao, and R.Z. Yuan, *Mater. Lett.*, **58**, 2654 (2004).
17. H. Zhang, L. Fang, T.H. Huang, R.Z. Yua, and R. Dronskowski, *J. Mat. Sci.*, **40**, 515 (2005).
18. H. Zhang, L. Fang, J.F. Yang, R.Z. Yuan, and H.X. Liu, *J. Mat. Sci: Mater. Electron.*, **15**, 327 (2004).
19. L. Fang, H. Zhang, J.F. Yang, R.Z. Yuan, and H.X. Liu, *Mater. Res. Bull.*, **39**, 677 (2004).
20. L. Fang, H. Zhang, T. H. Huang, H. X. Liu, R.Z. Yuan, *J. Mater. Sci.*, **39**, 1903 (2004).
21. H. Zhang, L. Fang, T.H. Huang, C.L. Diao, R.Z. Yuan, and R. Dronskowski, *J. Mat. Sci: Mater. Electron.*, **15**, 695 (2004).
22. R.D. Shannon, *Acta. Crystall.*, **A32**, 751 (1976).
23. J.A. Dean, *Lange's Handbook of Chemistry*, 15th ed. (McGraw-Hill, New York, 1999).
24. S.M. Pilgrim, A.E. Sutherland, and S.R. Winzer, *J. Am. Ceram. Soc.*, **73**, 3122 (1990).
25. M.R. Ranga Raju, and R.N.P. Choudhary, *J. Physics and Chemistry of Solids*, **64**, 847 (2003).