Dielectric properties and exploration of self-compensation mode of Tb in BaTiO₃ ceramics

Da-Yong LU¹ and Yan-Yan PENG

Research Center for Materials Science and Engineering, Jilin Institute of Chemical Technology, Jilin 132022, China

The self-compensation mode and dielectric properties of the nominal (Ba₁₋ₓTbₓ)(Ti₁₋₀.₅₀₇₉₅ₓTbₐ₀.₅₀₇₉₅)O₃ (0.05 ≤ x ≤ 0.20) ceramics (BTTT) were investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM), temperature-dependent Raman spectroscopy and electron paramagnetic resonance (EPR), dielectric and electrical measurements. The solid solution limit of Tb in BTTT was determined to be x = 0.12 by XRD. The variation in unit cell volume (Vₒ) with x satisfied Vegard’s law. In the case of Ba/Ti = 1, a complete self-compensation mode of Tb³⁺ in BaTiO₃ could not be formed like Eu³⁺ or Dy³⁺ because Tb ions in BTTT coexisted in the mixed-valence states of Ba-site Tb³⁺ and Ti-site Tb⁴⁺. The room-temperature resistivity decreased with increasing x owing to a gradually enhanced Tb³⁺ donor effect. An XSS specification with medium dielectric stability was achieved at x = 0.05. This ceramic is a promising dielectric for a higher room temperature permittivity (ε’ᵣₒ = 1190), a very low dielectric loss (tan δ < 0.02), and a nearly invariant ε’ in the frequency range of 10² to 10⁵ Hz.

Key-words: Tb-doped BaTiO₃, Dielectric, Self-compensation mode, Point defects, Electron paramagnetic resonance

1. Introduction

For rare earth-doped BaTiO₃ dielectric ceramics, four medium-sized rare earth elements with the atomic number (AN) from 63 to 66 in lanthanide, europium (Eu), gadolinium (Gd), terbium (Tb), and dysprosium (Dy), were reported to exhibit an amphoric behavior of substitutions for both Ba and Ti sites in the BaTiO₃ lattice.⁵⁻¹² Although when Ba/Ti > 1 Eu (AN = 63) can occupy Ba sites predominantly in the mixed valence states of Eu³⁺/⁴⁺ (4f⁷),¹) in the case of Ba/Ti = 1, 5% Eu doping may lead to a self-compensation mode of Eu³⁺ - Eu⁴⁺, where Eu ions exist completely as Eu³⁺.³) The experimental and theoretical studies indicate that Gd³⁺ (AN = 64, ⁴f³) shows a slight amphoric behavior,⁴⁻⁶ Dy (AN = 66, ⁴f⁵) has a stable valence state of +³,⁷⁻⁹ A high solid solution limit of x = 0.07 was discovered in (Ba₁₋ₓDyₓ)(Ti₁₋₀.₅₀₇₉₅ₓTbₐ₀.₅₀₇₉₅)O₃ with a self-compensation mode of Dy³⁺ - Dy⁴⁺.⁹) A temperature-stable Y⁷R specification with a room-temperature permittivity of ε’ᵣₒ = ~2400 was achieved in this ceramic.⁹)

Some researchers suggested that Tb (AN = 65, ⁴f³) occupies Ti sites as Tb³⁺ (⁴f³) in Ba-rich BaTiO₃.³⁻¹² However, our experiments in 2015 provided clear EPR evidence of existence of Tb³⁺ (⁴f³) at Ti sites, and in the case of Ba/Ti ≠ 1, Tb ions occupy both Ba and Ti sites in the mixed valence states of Tb³⁺/⁴⁺.³⁻⁵ A self-compensation mode with a stable valence state of +³ may exist in Eu- or Dy-doped BaTiO₃, where no valence change occurs.³⁻⁵ Tb lies at between Eu and Dy in AN. However, there is no any report about the self-compensation mode of Tb³⁺ - Tb⁴⁺ to date. Moreover, a high ε’ᵣₒ dielectric stability similar to the role of Dy doping³⁻⁵ is worthy of attention. In this work, the dielectric properties and self-compensation mode of Tb ions in BaTiO₃ were explored. A new XSS dielectric was achieved.

² Corresponding author: D.-Y. Lu; E-mail: dylu@jlict.edu.cn

2. Experimental procedure

BTTT ceramics were prepared using a solid state reaction method according to the formula (Ba₁₋ₓTbₓ)(Ti₁₋₀.₅₀₇₉₅ₓTbₐ₀.₅₀₇₉₅)O₃ (x = 0.05, 0.10, 0.11, 0.12, 0.15, 0.20). The starting materials BaCO₃ (99.4%) (Shanghai Zhizhen Chemical), TiO₂ (99.5%) (Shanghai Yuejiang Powders), and Tb₂O₃ (99.9%) (Shanghai Diyang Chemical) re-agent powders were weighed and carefully mixed. The mixture was calcinated in air at 1100°C for 5 h for decarbonation. The mixture with a PVA binder was then uniaxially pressed at 200 MPa for 2 min into pellets (φ12 mm). After sintered at 1400°C for 12 h in air, the pellets were densified into crack-free ceramics.

Powder X-ray diffraction (XRD) measurements were performed using an X-ray diffractometer (DX-2700, Dandong Haoyuan, China). All XRD data were collected between 20° ≤ 2θ ≤ 85° in steps of 0.02° at room temperature. Crystal structures and lattice parameters were determined by Pawley cell refinement using Reflex Package of MS Modeling (Accelry Inc., USA) and Cu Kα radiation (λ = 1.540562 Å). Raman spectrometer (LabRAM Xplora, Horiba Jobin Yvon, French) was equipped with a Linkam-600 heating/cooling stage for temperature-dependent Raman measurements at a laser excitation of 532 nm. SEM images were obtained using a scanning electric microscope (EVOMA 10, Zeiss, Germany), running at 15 kV. For electrical measurements, sintered disks were polished to a thickness of 0.8 mm. The samples were electroded with sputtered Au atoms and silver paste and then heat-treated at 500°C for 30 min. The dielectric and conducting properties of bulk ceramics were investigated at frequencies from 10 to 100 kHz using a Dielectric/Impedance spectrometer (Concept 41, Novocontrol, Germany) with an applied voltage of 1 V. Temperature-dependent electron paramagnetic resonance (EPR) measurements were performed using an X-band spectrometer (A300-10/12, Bruker, Germany), operating at 9.84 GHz. The gyromagnetic factor (γ) was calculated by the relationship hγ = gμB, where h is the
Planck constant \((h = 6.626 \times 10^{-34} \text{ J s})\), \(v_0\) is the microwave frequency, \(\beta\) is the Bohr magnetron \((\beta = 9.262 \times 10^{-23} \text{ J/T})\), \(H\) is the magnetic field strength.

3. Results and discussion

The room-temperature powder XRD patterns for \((\text{Ba}_{1-x}\text{Tb}_x)\)\((\text{Ti}_{1-y}\text{Tb}_y)\text{O}_3\) (BTTT) are shown in Fig. 1(a). BTTT ceramics with \(x \leq 0.12\) exhibited a tetragonal perovskite structure characteristic of two separate \((002)/(200)\) peaks [Fig. 1(c)], indicating that Tb ions were completely incorporated into the BaTiO\(_3\) lattice. A small amount of secondary phase appeared in the main perovskite phase when \(x \geq 0.13\). The solid solution limit of Tb in BTTT was determined to be \(x = 0.12\) by XRD. An interesting phenomenon is that this secondary phase was \(\text{Tb}_2\text{Ti}_2\text{O}_7\) for \(0.13 \leq x \leq 0.15\) but it converted to \(\text{Tb}_4\text{O}_7\) for \(x = 0.20\) [Fig. 1(b)], and the main perovskite phase for \(x \geq 0.15\) transformed to a cubic structure characteristic of a symmetric \((200)\) peak [Fig. 1(c)].

Figure 2 shows a plot of the unit cell volume \((V_0)\) as functions of \(x\) for the single-phase BTTT. The \(V_0\) of BTTT is greater than that of the tetragonal BaTiO\(_3\) (JCPDS cards: No. 5-626). This finding reveals that at least partial Tb ions entered Ti sites in BaTiO\(_3\). In the tetragonal region of \(x \leq 0.12\), \(V_0\) increases linearly with \(x\) for a continuous substitutional solid solution in which Tb ions should be randomly distributed in BTTT, or else some additional superlattice diffraction peaks would be detected.\(^{14,15}\) The \(V_0-x\) relationship satisfies Vegard's law.

On the basis of the BO\(_6\) octahedrons skeleton of the perovskite structure and a simple comparison between Tb and Ce\(^{4+}\) at Ti sites, where their coordinate Number (CN) is six, the 6-CN ionic radius of Tb\(^{4+}\), Tb\(^{3+}\), Ce\(^{4+}\), and Ti\(^{4+}\) are 0.76, 0.923, 0.87, and 0.605 Å, respectively.\(^{13,16,17}\) The \(V_0\) of \(x = 0.10\) BTTT sample (65.08 Å\(^3\)) is far less than that of Ba(Ti\(_{1-x}\)Ce\(_x\))O\(_3\) with \(x = 0.05\) \((V_0 = 66.37\text{ Å}^3)\),\(^{16}\) which implies that some Tb ions must occupy 12-CN Ba sites in light of a comparison in ionic size between Ba\(^{2+}\) (1.61 Å) and 12-CN Ti\(^{4+}\) (1.203 Å).\(^{13}\)

The room-temperature Raman spectra of BTTT are displayed in Fig. 3. The temperature-dependent Raman spectra of the \(x = 0.05\) sample are shown in Fig. 4. The Raman spectrum of the tetragonal BaTiO\(_3\) generally exhibits four typical bands peaking at 265, 305, 520, and 720 cm\(^{-1}\).\(^{18}\) They also appeared in BTTT.

![Fig. 1. Room-temperature Powder XRD patterns for (a) \(\text{Ba}_{1-x}\text{Tb}_x\)\((\text{Ti}_{1-y}\text{Tb}_y)\text{O}_3\) (BTTT), and XRD peaks in the vicinity of (b) 30° and (c) 45°.](image)

![Fig. 2. Plot of the unit cell volume \((V_0)\) as functions of \(x\) for BTTT. The data of the tetragonal and cubic BaTiO\(_3\) (JCPDS Cards No. 5-626 and 31-174) are given for comparison.](image)

![Fig. 3. Raman spectra of the single-phase BTTT ceramic powders.](image)

![Fig. 4. Temperature-dependent Raman spectra of the BTTT ceramic with \(x = 0.05\).](image)
The presence of a weak 305 cm$^{-1}$ mode is indicative of tetragonality of BTTT at room temperature, which is in good agreement with the above XRD results. The 305 cm$^{-1}$ band gradually merged into the main 265 cm$^{-1}$ band above 120°C, which implies that the tetragonal–cubic (t–c) phase transition occurred at between 120 and 135°C. An additional band appeared and its peak position red-shifted from 829 to 806 cm$^{-1}$ with increasing $x$. This band originates from the Raman charge effect, indicating an increase in the number of Tb$^{3+}$ ions incorporated into the BaTiO$_3$ lattice.

Figure 5 shows the SEM images of BTTT. No secondary phase was observed for $x \leq 0.12$. The bulk density (5.65 g/cm$^3$) is nearly $x$-independent. This density reaches 93% of theoretical density of BTTT. The $x = 0.05$ sample exhibited a non-uniform microstructure consisting of fine grains (0.5–2 μm) and coarse grains (3–15 μm), as seen in Figs. 5(a) and 5(b). For $0.10 \leq x \leq 0.12$, the samples tended to homogenous grain growth and their mean grain size was approximately 3 μm [Figs. 5(c) and 5(d)]. This reveals that Tb doping cannot refine grains and suppress grain growth.

The evolution in EPR signals as a function of temperature ($T$) for BTTT is shown in Fig. 6. At $T = 30$ and 90°C, the EPR spectra of the $x = 0.05$ sample mainly exhibited four EPR signals: (1) a signal with $g = 1.974$ was attributed to ionized Ba-vacancy defects (VBa); (2) a weaker signal with $g = 2.004$ was attributed to ionized Ti-vacancy defects (VTi); (3) a broad signal at $g = 5.94$ originated from Tb$^{4+}$ Kramers ions at Ti sites; and (4) a very weak sextet signal originated from Mn$^{2+}$ impurities in ceramic. As $T$ was increased to 150°C, both VTi- and Mn$^{2+}$ sextet signals were activated, which implies occurrence of the t–c phase transition. The VBa-related signal is nearly temperature-independent [Fig. 6(a)]. It can be seen from Fig. 6 that both intrinsic Ba and Ti vacancies may coexist in the main perovskite lattice.

As $x$ was increased to 0.10, only two signals associated with VTi and Tb$^{4+}$ were observed, and both VBa-related and Mn$^{2+}$ sextet signals disappeared. The $g = 5.94$ signal was obviously broadened because of an increase in Tb doping level. A slight activation of VTi-related signal reveals that the t–c phase transition occurred at between 90 and 120°C. The persistence of VTi-related signal from $x = 0.05$ to 0.10 suggests that some Tb$^{4+}$ ions substituted for Ba sites in BTTT, because trivalent rare earth ions at Ba sites always induces Ti vacancies. Thus, it can be deduced that Tb ions occupied both Ba and Ti sites in the mixed valence states of Tb$^{4+}$/Tb$^{3+}$ and the self-compensation mode of Tb$^{3+}_{Ba}$ – Tb$^{3+}_{Ti}$ could not be formed in BTTT.

Figure 7 shows the temperature dependences of dielectric permittivity ($\varepsilon'$) and dielectric loss (tan δ) for BTTT, measured at 1 kHz. It has been known that BaTiO$_3$ shows a first-order phase transition (FPT) behavior with a sharp peak in $\varepsilon'$-$T$ curve, and the temperatures that the FPT phase transition (i.e. the Curie point $T_C$) occurs are 121 and 130°C for BaTiO$_3$ single crystal and coarse-grained ceramic, respectively. The $T_C$ of BaTiO$_3$ generally relates to the preparation routes, ceramic microstructure, and heating rate or cooling rate during dielectric measurement. The $T_C$ of BaTiO$_3$ may change slightly because of the existence of
thermal relaxation effect during heating and cooling.\textsuperscript{18} The $\varepsilon \sim T$ curve of the $x = 0.05$ sample showed a FPT behavior similar to BaTiO$_3$, but $T_C = 132^\circ$C implies that 5\% Tb doping resulted in a slight shift of $T_C$ of BaTiO$_3$ towards high temperature. When $x > 0.05$, BTTT exhibited a so-called “diffusion of ferroelectric phase transition” (DPT) around $T_m$ [$T_m$ representing the temperature at which maximum permittivity ($\varepsilon''_m$) occurs]. For relaxor-type materials, $T_m$ does not longer correspond to the phase transition of material with DPT in the substance. As shown in Fig. 8, the temperature dependences of $\varepsilon'$ for the $x = 0.12$ BTTT sample at different frequencies suggest that the 12\% Tb-doped BaTiO$_3$ sample is a relaxor-type material, i.e., the $T_m$ increases with frequency from 78\%C at 10$^2$Hz to 90\%C at 10$^5$Hz. With increase in $x$, $T_m$ moved downwards due to Tb doping, as seen in Fig. 7(a). This abnormal regularity in $T_m$ shift suggests that the rate of Ba-site Tb$^{3+}$ to Ti-site Tb$^{4+}$ in BTTT was variable and complete Tb$^{3+}$-Tb$^{4+}$ defect complexes could not be formed. This phenomenon also occurred for multisite occupation of Ca in the BaTiO$_3$-CaTiO$_3$ solid solution, where a systematic increase in Ti-site occupancy and then the Ti-site occupancy is invariant and the Ba-site occupancy of Ca becomes dominant.\textsuperscript{25-27}

The orthorhombic-tetragonal ($e$-c) phase transition ($T_2$) of BaTiO$_3$ occurs at approximately 10$^5$C and corresponds to a weaker dielectric peak.\textsuperscript{23,24} This peak of the $x = 0.05$ sample broadened significantly and flattened below 85\%C in $\varepsilon \sim T$ curve so that this sample satisfied XSS specification, i.e., $|\varepsilon' - \varepsilon''| < |\varepsilon''|$ in the range of $-55$ to 85\%C, and its room-temperature permittivity ($\varepsilon''_{RT}$) reached 1190. At $x = 0.10$, the dielectric peak had a bimodal distribution, which was caused by a downward shift in $T_m$ (main peak) and an upward shift in $T_2$ (shoulder peak). When $x = 0.11$ and 0.12, two samples exhibited a more diffused diffuse phase transition (DPT)\textsuperscript{29,30} behavior. The $T_m$ of the $x = 0.15$ sample was 5$^\circ$C lower than that of the $x = 0.12$ sample, implying a decrease in Tb content in the lattice. This result coincides with presence of a secondary phase of Tb$_2$Ti$_2$O$_7$ observed by XRD.

In the XSS temperature region, the $x = 0.05$ sample exhibited a much lower dielectric loss (tan $\delta < 0.02$), as seen in Fig. 7(b). The tan $\delta$ gradually increased with increasing $x$. This changing trend reverses the change in resistivity ($\rho$) for BTTT (Fig. 9). A plot of the room temperature resistivity ($\rho_{RT}$) as functions of $x$ for BTTT is shown in Fig. 10. In the tetragonal region, the $\rho_{RT}$ shows a linear fall from $1.0 \times 10^8$ to $1.7 \times 10^7\Omega$cm with $x$, implying that the Tb$^{3+}$ donor effect was enhanced. The $\rho_{RT}$ relation for BTTT under a DC (Direct Current) voltage of 40 V is shown in Fig. 11. The $\rho_{RT}$ increased rapidly by two orders of magnitude compared to the case of AC (Alternating Current) (Fig. 10). This implies that the Tb$^{3+}$ donor effect is very weaker and the valence state change of Ti-site Tb$^{3+}$ to Tb$^{4+}$ contributes to high resistivity under DC voltage.

For the $x = 0.05$ XSS dielectric, its frequency ($f$) dependences of $\varepsilon'$ and tan $\delta$ at different temperatures were investigated, as shown in Fig. 12, where the inset depicts the $\rho$-$f$ curve. The $\varepsilon'$ at each temperature ($T$) remained almost constant in the frequency range of 10$^2$ to 10$^5$Hz [Fig. 12(a)]. This behavior is similar to the dielectric-frequency stability in the giant dielectric constant material CaCu$_3$Ti$_4$O$_{12}$.\textsuperscript{29,30,32} The $\delta$ of the $\varepsilon'$ at $T > 10^5$Hz, with the decrease in $f$, tan $\delta$ at each $T$ increased and gradually dispersed, but tan $\delta$ at higher $T$ increased rapidly [Fig. 12(b)]. The trend of $\rho$-$f$ curve is opposed to that of tan $\delta$-$f$ curve (Fig. 12 inset).

The above EPR investigations indicate that Tb ions in BTTT exhibit a self-adjustable amphoteric behavior with the mixed valence states of Tb$^{3+}$ and Tb$^{4+}$ utilized to preserve lattice structure.
concentration of $\text{Eu}$ in BTTT is responsible for an increase in $\tan \beta$ effect. The complete formation of the self-compensation mode of room temperature resistivity ($\rho_{\text{RT}}$) ($\text{Tb}^3$ site $\text{Tb}^4$ ions) at Ba sites induce Ti vacancies by means of $4\text{Tb}^3_0 \rightarrow \text{V}_{\text{Ti}}^{\text{m}}$. This is the reason that Ti vacancies persist in BTTT. Except for $\text{V}_{\text{Ti}}^{\text{m}}$-created $\text{Tb}^3$ ions, the excess of $\text{Tb}^3$ ions ($\delta$) residue in BTTT is responsible for an increase in $\tan \delta$ and a decrease in $\rho_{\text{RT}}$ with increasing $x$ (Figs. 7–11) because of the $\text{Tb}^3_0$ donor effect. The complete formation of the self-compensation mode of $\text{Tb}^3_0 - \text{Tb}^3$ is impossible. The real formula of BTTT is inferred to be described as $(\text{Ba}_{1-x}\text{Tb}^{3+y}\text{Ti}_{1-x}\text{Tb}^{3+y}\text{V}_{\text{Ti}}^{\text{m}})(\text{Ba}_{1-x}\text{Tb}^{3+y}\text{V}_{\text{Ti}}^{\text{m}})\text{O}_3$

4. Conclusions

In conclusion, the nominal $(\text{Ba}_{1-x}\text{Tb}_x)(\text{Ba}_{1-x}\text{Tb}_x)\text{O}_3$ ($x = 0.12$) ceramics (BTTT) with a tetragonal perovskite structure can be prepared using a solid state reaction method. The solid solution limit of $\text{Ti}$ in BTTT is determined to be $x = 0.12$ by XRD. The unit cell volume ($V_0$) as functions of $x$ satisfies Vegard’s law. $\text{Ti}$ ions is not a good grain growth inhibitor. For $\text{Ti}$ doping ions, in the case of $\text{Ba}/\text{Ti} = 1$, a complete self-compensation mode of $\text{Ba}^{2+} - \text{Ti}^{4+}$ cannot be formed in the main $\text{BaTiO}_3$ lattice like $\text{Eu}^{2+} - \text{Eu}^{3+}$ or $\text{Dy}^{2+} - \text{Dy}^{3+}$ $\text{Ti}$ ions in BTTT exhibit a self-adjustable anisotropic behavior with the mixed valence states of $\text{Ti}^{3+}$ and $\text{Ti}^{4+}$ utilized to preserve lattice electroneutrality. The room temperature resistivity ($\rho_{\text{RT}}$) shows a linear fall from 1.0 x $10^4$ to 1.7 x $10^2$ $\Omega\cdot$cm with $x$ owing to a gradually enhanced $\text{Ti}^{3+}$ donor effect. The $x = 0.05$ BTTT sample exhibits some advantages of higher $\varepsilon’_{\infty}$ (1190), lower $\tan \delta$ (< 0.02), and nearly invariant $\varepsilon’$ over the frequency range $10^2$ to $10^5$ Hz. This ceramic is a promising candidate for X5S dielectric application.

Acknowledgment This work was supported by the projects of the National Natural Science Foundations of China (Grant No. 21271084) and Jilin Province.

References

1) D.-Y. Lu, M. Sugano, X.-Y. Sun and W.-H. Su, Appl. Surf. Sci., 242, 318–325 (2005).
2) D.-Y. Lu, T. Koda, H. Suzuki and M. Toda, J. Ceram. Soc. Japan, 113, 721–727 (2005).
3) D.-Y. Lu, T. Ogata, H. Unuma, X.-C. Li, N.-N. Li and X.-Y. Sun, Solid State Ionics, 201, 6–10 (2011).
4) T. Takeda, J. Phys. Soc. Jpn., 24, 533–542 (1968).
5) M. T. Buscaglia, V. Buscaglia, M. Viviani, P. Nanni and M. Hanuskaova, J. Eur. Ceram. Soc., 20, 1997–2007 (1999).
6) L.-X. Xue, Y. Chen and R. J. Brook, Mater. Sci. Eng., B, 1, 193–201 (1988).
7) Y. Tsur, A. Hitomi, I. Scrymgeour and C. A. Randall, Jpn. J. Appl. Phys., 40, 255–258 (2001).
8) E. J. Lee, J. Jeong and Y. H. Han, Jpn. J. Appl. Phys., 43, 8126–8129 (2004).
9) D.-Y. Lu and S.-Z. Cui, J. Eur. Ceram. Soc., 34, 2217–2227 (2014).
10) M. T. Buscaglia, V. Buscaglia, M. Viviani and P. Nanni, J. Am. Ceram. Soc., 84, 376–384 (2001).
11) Y.-X. Li, X. Yao, X.-S. Wang and Y.-B. Hao, Ceram. Int., 38, S29–S32 (2012).
12) Y. Tsur, T. D. Dunbar and C. A. Randall, J. Electroceram., 7, 25–34 (2001).
13) D.-Y. Lu, Solid State Ionics, 276, 98–106 (2015).
14) J. Chen, H. M. Chan and M. P. Harmer, J. Am. Ceram. Soc., 72, 593–598 (1989).
15) Y. Inaguma, J.-H. Sohn, I. S. Kim, M. Itoh and T. Nakamura, J. Phys. Soc. Jpn., 278, 3831–3832 (1992).
16) D.-Y. Lu, M. Sugano and M. Toda, J. Am. Ceram. Soc., 89, 3112–3123 (2006).
17) R. D. Shannon, Acta Crystallogr. A, 32, 751–767 (1976).
18) D.-Y. Lu, X.-Y. Sun and M. Toda, J. Phys. Chem. Solids, 68, 650–664 (2007).
19) D.-D. Han, D.-Y. Lu and X.-Y. Sun, J. Alloys Compd., 576, 24–29 (2013).
20) M. Chkhechek and M. Maglione, J. Phys. Condens. Matt., 6, 10159–10170 (1994).
21) T. Kolodiazhnii and A. Petric, J. Phys. Chem. Solids, 64, 953–960 (2003).
22) D.-Y. Lu, W. Cheng, X.-Y. Sun and Q.-L. Liu, J. Raman Spectrosc., 45, 963–970 (2014).
23) M. L. Mulvihill, K. Uchino, L. Zhang and W.-W. Cao, Philos. Mag. B, 74, 25–36 (1996).
24) D. Hennings, Int. J. High Tech. Ceram., 3, 91–111 (1987).
25) Z. Q. Zhuang, M. F. Hamer and D. M. Smyth, Mater. Res. Bull., 22, 1329–1335 (1987).
26) P. S. R. Krishna, D. Pandey, V. S. Tiwari, R. Chakravathy and B. A. Dasannacharya, Appl. Phys. Lett., 82, 231–233 (1993).
27) S. Lee and C. A. Randall, Appl. Phys. Lett., 92, 111904 (2008).
28) D. Hennings, A. Schnell and G. Simon, J. Am. Ceram. Soc., 65, 539–544 (1982).
29) M. A. Subramanian, D. Li, N. Duan, B. A. Reosner and A. W. Sleight, J. Solid State Chem., 151, 323–325 (2000).
30) T. B. Adams, D. C. Sinclair and A. R. West, Adv. Mater., 14, 1321–1322 (2002).
31) J. Liu, R. W. Smith and W.-N. Mei, Chem. Mater., 19, 6020–6024 (2007).
32) P. Thongbai, B. Putasaeng, T. Yamwong and S. Maensiri, J. Alloys Compd., 509, 7416–7420 (2011).