J Mater Sci: Mater Electron (2016) 27:4201–4205
DOI 10.1007/s10854-016-4283-1

Microwave dielectric properties of $ZnO–Nb_2O_5–xTiO_2$ ceramics prepared by reaction-sintering process

Pan Ruan[1] · Peng Liu[1] · Bao-chun Guo[1] · Feng Li[1] · Zhi-fen Fu[1]

Received: 17 October 2015 / Accepted: 2 January 2016 / Published online: 30 January 2016

Abstract The $ZnO–Nb_2O_5–xTiO_2$ ($1 \leq x \leq 2$) ceramics were fabricated by reaction-sintering process, and the effects of TiO_2 content and sintering temperature on the crystal structure and microwave dielectric properties of the ceramics were investigated. The XRD patterns of the ceramics showed that $ZnTiNb_2O_8$ single phase was formed as $x \leq 1.6$ and second phase $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ appeared at $x \geq 1.8$. With the increase of TiO_2 content and sintering temperature, the amount of the second phase $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ increased, resulting in the increase of dielectric constant, decrease of $Q \times f$ value, and the temperature coefficient of resonant frequency (τ_f) shifted to a positive value. The optimum microwave dielectric properties were obtained for $ZnO–Nb_2O_5–2TiO_2$ ceramics sintered at 1075 °C for 5 h: $\varepsilon_r = 45.3$, $Q \times f = 23{,}500$ GHz, $\tau_f = +4.5$ ppm/°C.

1 Introduction

The rapid growth of satellite and personal mobile communications has resulted in the need for narrow band, temperature-stable materials that operate at high frequencies. To utilize these, low-loss materials with moderate dielectric constant (ε_r) characteristics and near-zero temperature coefficients of resonant frequency (τ_f) are required [1–3].

Among the numerous dielectric materials, the $ZnTiNb_2O_8$ ceramics with a fully disordered α-PbO_2 structure were first described by Baumgarte and Blachnik [4, 5], and its microwave dielectric properties were investigated by Kim et al. [6] as follows: ε_r of 34.3, τ_f of −52 ppm/°C, and $Q \times f$ of 42,500 GHz sintered at a high temperature (1250 °C). Mei et al. [7] reported that nanosize $ZnTiNb_2O_8$ precursors powders could be obtained at 700 °C by an aqueous sol–gel process and the ceramics sintered at 1050 °C showed excellent microwave properties with ε_r of 35.3, $Q \times f$ value of 66,700 GHz, and τ_f of −55.4 ppm/°C. In addition, the large negative temperature coefficient of resonant frequency of $ZnTiNb_2O_8$ limited its application. Generally speaking, the adjusting of τ_f to near-zero value may be achieved by adding other compounds with positive τ_f [8] and TiO_2 ($\tau_f = +450$ ppm/°C) has been usually used to tune the temperature coefficient [9]. Kim et al. [6, 10] reported that the $(1 - x)$ $ZnNb_2O_6–xTiO_2$ system with $x = 0.58$ had a near-zero τ_f value and a large ε_r (45), however, the quality factor was low ($Q \times f = 6000$ GHz).

Reaction-sintering process is a simple and effective route to synthesize ceramics, which makes the chemical reaction process completed in sintering step which should be done during the calcination step. Reaction-sintering process saves a lot of energy, time, and avoid grinding fine steps after the calcination craft which could introduce impurities, so that it has great application value in the practical production. In this work, the $ZnO–Nb_2O_5–xTiO_2$ ceramics were fabricated by reaction-sintering process, and the effects of TiO_2 on the microstructures, phase compositions, and microwave dielectric properties were investigated.

✉ Peng Liu
liupeng@snnu.edu.cn

[1] School of Physics and Information Technology, Shaanxi Normal University, Xi'an 710119, China

2 Experimental procedures

All samples in this study were prepared from high-purity oxide powders (≥99 %), appropriate amounts of raw materials for stoichiometric $ZnO + Nb_2O_5 + xTiO_2$ ($1 \leq x \leq 2$) were milled in ethanol with ZrO_2 balls for 12 h. After dried and pulverized the slurry, the powders were then pressed into pellets with 11.5 mm in diameter and 5.5 mm in thickness. The specimens were sintered from 1000 to 1150 °C for 5 h in air with a heating rate of 3 °C/min.

The bulk densities of the sintered ceramics were measured by the Archimedes method. The crystal structures were analyzed using X-ray diffraction (XRD) with Cu Ka radiation (Rigaku D/MAX2550, Japan). Microstructures of the ceramics were performed by scanning electron microscope (FEI Co. Eindhoven, Netherlands). The microwave dielectric properties of the samples at microwave frequency were measured by the $TE_{01\delta}$ shielded cavity method with a vector network analysis (ZVB20, Rohde & Schwarz, Germany). The temperature coefficient of resonant frequency (τ_f) were calculated with the following equation:

$$\tau_f\ (\text{ppm}/^{\circ}\text{C}) = \frac{f_{80} - f_{25}}{f_{25} \times (80 - 25)} \times 10^6 \quad (1)$$

where f_{80} and f_{25} were the $TE_{01\delta}$ resonant frequency measured at 80 and 25 °C, respectively.

3 Results and discussions

The XRD patterns of $ZnO–Nb_2O_5–xTiO_2$ ($x = 1$, 1.4, 1.6, 1.8, 2) ceramics sintered at 1075 °C are shown in Fig. 1. As $x \leq 1.6$, a single-phase $ZnTiNb_2O_8$ (JCPDS #88-1973) is obtained. As shown in the insert of Fig. 1, the main peak (111) shift slightly toward higher angles with the increase of TiO_2 content and almost no longer move for $x \geq 1.6$, indicating a decrease of unit-cell volume due to the substitution of Ti^{4+} ions (0.605 Å) for Nb^{5+} ions (0.640 Å) of $ZnTiNb_2O_8$ [11]. Thus, the solid solution is supposed to be formed for $x \leq 1.6$. The chemical reaction happens between excess TiO_2 and $ZnTiNb_2O_8$, resulting in a new phase $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ (ICDD–PDF#39-0291) [11] for the samples with $x \geq 1.8$. Figure 2 shows the XRD patterns of $ZnO–Nb_2O_5–2TiO_2$ sintered at temperatures from 1000 to 1150 °C. Regardless of sintering temperature, two types of phase are obtained in all samples and the peak intensities of $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ phase gradually enhance with increasing sintering temperature. This indicates that both TiO_2 content and sintering temperature affect the generation of $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ phase, which ultimately affect the dielectric properties of the composite ceramics.

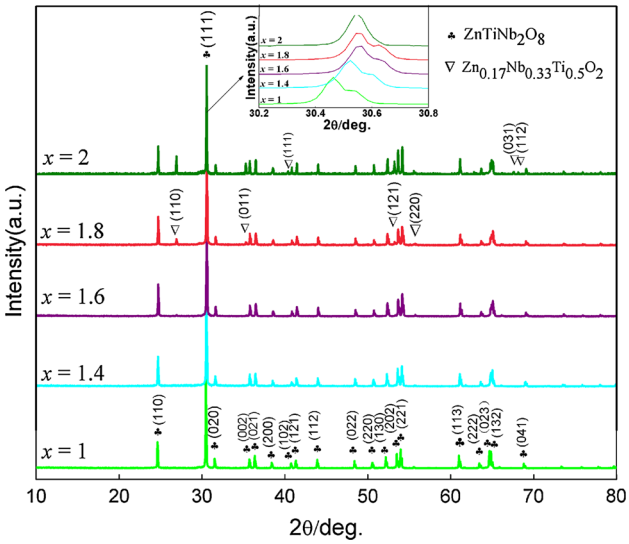

Fig. 1 X-ray diffraction patterns of $ZnO–Nb_2O_5–xTiO_2$ ($1 \leq x \leq 2$) sintered at 1075 °C

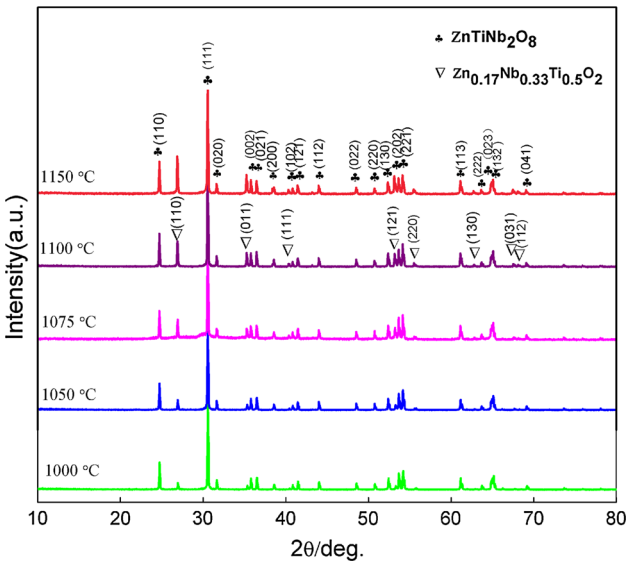

Fig. 2 X-ray diffraction patterns of $ZnO–Nb_2O_5–2TiO_2$ sintered at different temperature

Figure 3 shows the bulk densities of $ZnO–Nb_2O_5–xTiO_2$ ($1 \leq x \leq 2$) ceramics sintered at different temperatures. The bulk densities of $ZnTiNb_2O_8$ ($x = 1$) ceramic increase initially and reach a maximum (5.23 g/cm^3) at 1075 °C (relative density corresponding to 98.05 %), then slightly decrease with the increase of temperature, which means $ZnTiNb_2O_8$ have a nearly full density sintered at 1075 °C for 5 h, 175 °C lower than that by a conventional solid-state method [6]. As shown in Fig. 3, at the fixed temperature (≥1025 °C), the bulk densities of the ceramics decrease with addition of TiO_2 since TiO_2 and

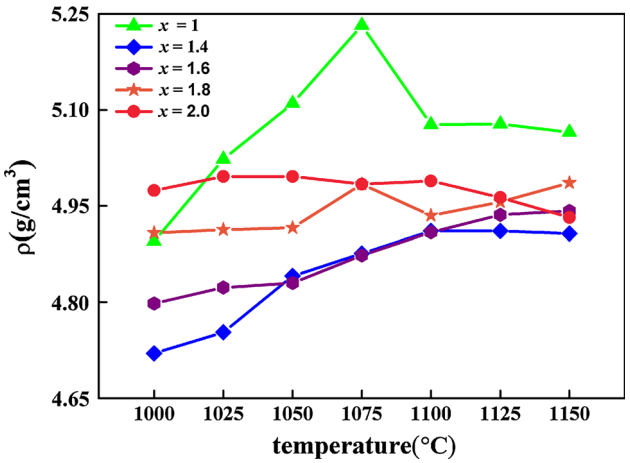

Fig. 3 The bulk densities of $ZnO–Nb_2O_5–xTiO_2$ ceramics sintered at different temperatures

$Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ have lower densities (4.25 and 4.90 g/cm^3, respectively) than that of $ZnTiNb_2O_8$ (5.33 g/cm^3).

Figure 4 shows the SEM images of $ZnO–Nb_2O_5–xTiO_2$ ($1 \leq x \leq 2$) ceramics sintered at 1075 °C. In order to obtain the average grain size, the statistics of grain size were calculated on the more than 300 particles in each sample. It can be seen that all samples exhibit a compact microstructure, while the average grain size increase from 3.42 to 7.23 μm (Fig. 2a, b) and then decrease to 2.81 μm for $x = 2$(Fig. 2e). It was suggested that excess TiO_2 promote the grow of the grains, but the second phase $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ restrain the crystal move that led the decrease of grain size [12, 13].

Figure 5 demonstrates the dielectric constant of $ZnO–Nb_2O_5–xTiO_2$ ($1 \leq x \leq 2$) ceramics sintered at different temperatures. As is well known, the dielectric constant is dependent on the density, secondary phases, and the crystal

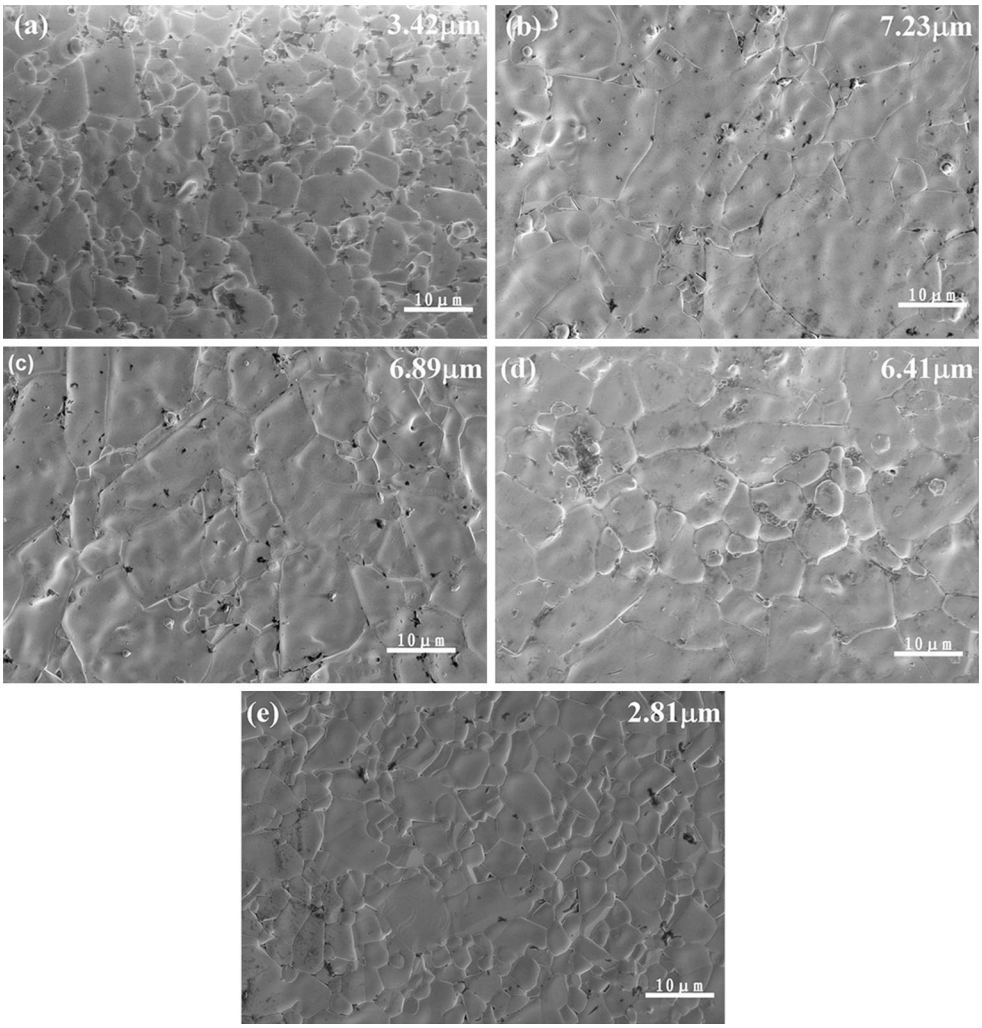

Fig. 4 The SEM images of $ZnO–Nb_2O_5–xTiO_2$ samples sintered at 1075 °C for 5 h with different x: **a** $x = 1$, **b** $x = 1.4$, **c** $x = 1.6$, **d** $x = 1.8$, **e** $x = 2.0$

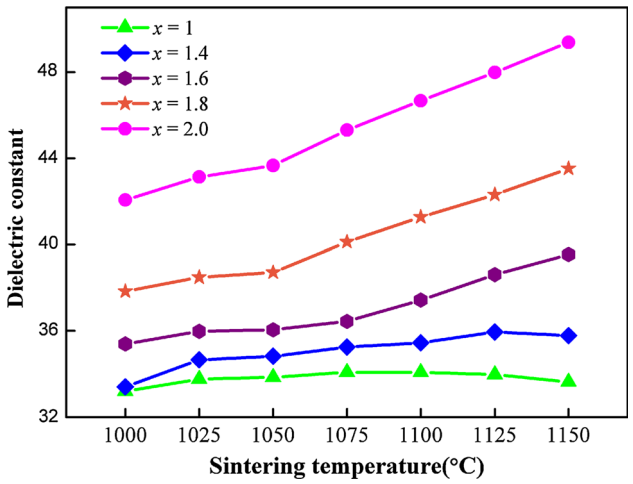

Fig. 5 The dielectric constant of ZnO–Nb_2O_5–$xTiO_2$ ($1 \leq x \leq 2$) ceramics sintered at different temperatures

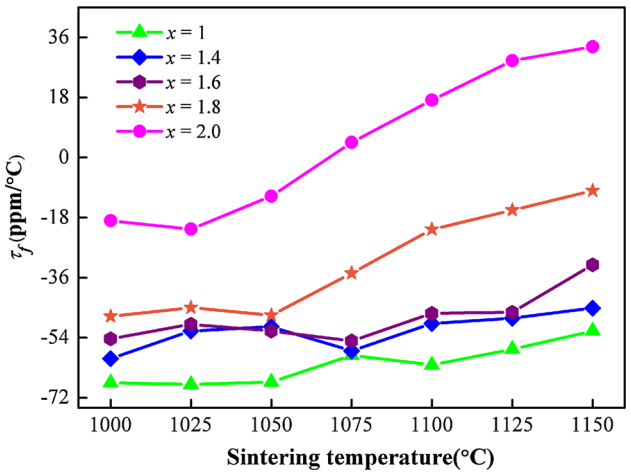

Fig. 7 The τ_f values of ZnO–Nb_2O_5–$xTiO_2$ ($1 \leq x \leq 2$) ceramics sintered at different temperatures

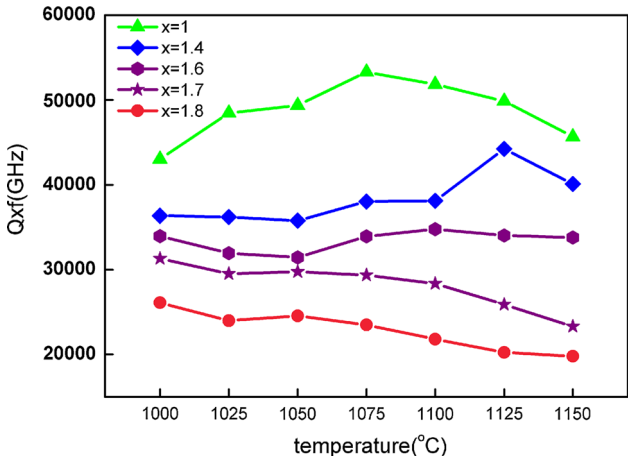

Fig. 6 The $Q \times f$ values of ZnO–Nb_2O_5–$xTiO_2$ ($1 \leq x \leq 2$) ceramics sintered at different temperatures

structure in microwave frequency [14]. The variation trend of ε_r values of the samples are in accordance with that of the corresponding density for $x \leq 1.4$. Furthermore, ε_r values increase with increasing TiO_2 content and sintering temperatures. It is suggested that the $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ ($\varepsilon_r = 95$) [15] content is the dominating factor to control dielectric constant which is consistent with the logarithmic mixing rule [16]:

$$\ln \varepsilon_r = \upsilon_1 \ln \varepsilon_{r1} + \upsilon_2 \ln \varepsilon_{r2} \quad (2)$$

where ε_{r1} and ε_{r2} are the dielectric constant of $ZnTiNb_2O_8$ and $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$; υ_1 and υ_2 are their volume fraction.

Figure 6 presents the $Q \times f$ values of ZnO–Nb_2O_5–$xTiO_2$ ($1 \leq x \leq 2$) ceramics sintered at different temperatures. The relationships between $Q \times f$ values and sintering temperatures follow the similar trend to those between density and sintering temperature for $x = 1$. While the $Q \times f$ values of ZnO–Nb_2O_5–$xTiO_2$ seem to decrease firstly and then increase for $1.4 \leq x \leq 1.6$, owing to the increase of the TiO_2 content that cause the increase in lattice defects, but higher sintering temperature is beneficial to promote the densification and crystallizability of the ceramics which ultimately make the $Q \times f$ values increase. However, the $Q \times f$ value of all samples exhibits the same tendency of decline when $x \geq 1.8$, because the raising in TiO_2 content and sintering temperature would be helpful to the generation of $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ phase, which have an imponderable impact on crystal structure. Furthermore, the $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ phase have a relatively lower $Q \times f$ value (15,000 GHz) [15] than that of $ZnTiNb_2O_8$ ceramics ($Q \times f$ value of 56,900 GHz) [17].

As x changes from 1 to 2, τ_f values varied from −70 to 30 ppm/°C in Fig. 7. A near-zero τ_f value is obtained at $x = 2$. For a given temperature (such as 1075 °C), it can be seen that the τ_f values almost have no change with x varies from 1 to 1.6 but dramatically shift to a positive value when $x \geq 1.8$, and the phenomenon support the transformation process of phases as indicated in the XRD patterns: $x \leq 1.6$, Ti^{4+} ions have entered the lattice of $ZnTiNb_2O_8$ leading to the decrease of actual TiO_2 content thus have no obvious contribution to the adjustment of τ_f value. While when $x \geq 1.8$, the τ_f values are observed to increase with increasing TiO_2 content and sintering temperature is reasonable when considering the difference in reported τ_f values of $ZnTiNb_2O_8$ and $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ (−56 and +237 ppm/°C [15], respectively) on the basis of the mixing rule for composite materials. The good microwave dielectric properties of $\varepsilon_r = 45.3$, $Q \times f = 23{,}500$ GHz, $\tau_f = +4.5$ ppm/°C were obtained for ZnO–Nb_2O_5–$2TiO_2$ specimen sintered at 1075 °C for 5 h.

4 Conclusion

The crystal structure and microwave dielectric properties of $ZnO–Nb_2O_5–xTiO_2$ ceramics ($x = 1$, 1.4, 1.6, 1.8, 2) synthesized by reaction-sintering process. The superior microwave dielectric properties were obtained for $ZnTiNb_2O_8$ ceramics sintered at 1075 °C for 5 h: $\varepsilon_r = 34.1$, $Q \times f = 53{,}300$ GHz, $\tau_f = -59.3$ ppm/°C. While with increasing TiO_2 content and sintering temperature, the content of the second phase $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ gradually increased, which was helpful to increase the dielectric constant and τ_f value. The excellent microwave dielectric properties were obtained for $ZnO–Nb_2O_5–2TiO_2$ ceramics sintered at 1075 °C for 5 h: $\varepsilon_r = 45.3$, $Q \times f = 23{,}500$ GHz, $\tau_f = +4.5$ ppm/°C.

Acknowledgments This work is supported by the National Natural Science Foundation of China (Grant Nos: 51272150 and 51572162) and Specialized Research Fund for the Doctoral Program of Higher Education (No. 20120202110004) and the Fundamental Research Funds for the Central Universities (GK201401003).

References

1. H.W. Lee, J.H. Park, J.S. Nahm, D.W. Kim, J.G. Park, Mater. Res. Bull. **45**, 21 (2010)
2. H. Jantunen, R. Rautioaho, A. Unsimäki, S. Leppävuori, J. Eur. Ceram. Soc. **20**, 2331 (2000)
3. L. Fang, Q. Yu, C. Hu, H. Zhang, Mater. Lett. **61**, 4140 (2007)
4. A. Baumgarte, R. Blachnik, Mater. Res. Bull. **27**, 1287 (1992)
5. A. Baumgarte, R. Blachnik, J. Alloys Compd. **210**, 75 (1994)
6. D.W. Kim, D.Y. Kim, K.S. Hong, J. Mater. Res. **15**(6), 1331 (2000)
7. Q.J. Mei, C.Y. Li, J.D. Guo, H.T. Wu, J. Alloys Compd. **626**, 217 (2015)
8. M.P. Seabra, A.N. Salak, V.M. Ferreira, J.L. Ribeiro, L.G. Vieira, J. Eur. Ceram. Soc. **24**, 2995 (2004)
9. J. Ortiz-Landeros, M.E. Contreras-Garcia, C. GomezYanez, J. Solid State Chem. **184**, 1304 (2011)
10. D.W. Kim, K.H. Ko, D.K. Kwon, J. Am. Ceram. Soc. **85**(5), 1169 (2002)
11. S.P. Wu, J. Ni, J.H. Luo, X.H. Ding, Mater. Chem. Phys. **117**, 307 (2009)
12. Y.-C. Liou, C.-Y. Shiue, J. Eur. Ceram. Soc. **29**, 1165 (2009)
13. T.K. Chen, W.B. Ma, R. Li, J. Mater. Sci.: Mater. Electron. **25**, 2494 (2014)
14. H.F. Zhou, X.B. Liu, X.L. Chen, L. Fang, H. Wang, J. Mater. Sci.: Mater. Electron. **23**, 238 (2012)
15. D.W. Kim, J.H. Kim, J.R. Kim, K.S. Hong, Jpn. J. Appl. Phys. **40**, 5994 (2001)
16. K.P. Surendran, N. Santha, P. Mohanan, Eur. Phys. J. B **41**, 301 (2004)
17. Q.W. Liao, L.X. Li, X. Ren, Mater. Lett. **89**, 351 (2012)