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Microwave dielectric properties and low temperature sintering behavior of $Li_2CoTi_3O_8$ ceramic

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ABSTRACT

The microwave dielectric properties of Li-containing cubic spinel $Li_2CoTi_3O_8$ have been investigated. Single-phase powders can be synthesized from the mixed-oxide route at 900 °C and dense ceramics (~97% of the theoretical density) with uniform microstructures (6–15 μm) can be obtained by sintering in air at 1025 °C. The ceramic exhibits a moderate permittivity (ε_r) of 28.9, a high quality factor value ($Q \times f$) of 52,600, and a low temperature coefficient of the resonant frequency (τ_f) of 7.4 ppm/°C. The addition of $BaCu(B_2O_5)$ (BCB) can effectively lower the sintering temperature of $Li_2CoTi_3O_8$ ceramic from 1025 °C to 900 °C and does not induce much degradation of the microwave dielectric properties. The BCB doped $Li_2CoTi_3O_8$ ceramic can be compatible with Ag electrode, which makes it a promising ceramic for LTCC technology application.

1. Introduction

In the last few decades, the microwave-based wireless communications industry has been revolutionized with the continuing requirement of miniaturization. Dielectric resonators (DRs) provide significant advantages in terms of compactness, light weight, temperature stability and relatively low cost in the production of high frequency devices. For application to resonators, microwave dielectric materials require a high relative permittivity (ε_r) to facilitate circuit miniaturization, a high quality factor values ($Q \times f$) to increase their selectivity, and a near-zero temperature coefficient of the resonant frequency (τ_f) to ensure the stability of the frequency against temperature changes [1]. Although some materials with excellent properties have been developed for commercial applications, such as $Ba(Mg_{1/3}Ta_{2/3})O_3$, $(Zr,Sn)TiO_4$, and $CaTiO_3$–$NdAlO_3$ [1], active work is still being carried out in search of sophisticated materials to perform the same or an improved function [2–7].

Recently, there is a considerable interest in lowering the sintering temperatures of dielectric ceramics for co-firing with cheaper and highly conductive internal electrode metals such as Ag (the melting point 961 °C) and Cu (the melting point 1050 °C) [7,8], however, the sintering temperatures of most of commercial microwave dielectric ceramics are usually above 1300 °C. In order to reduce the sintering temperature of dielectric ceramics, there are several methods commonly explored [9]: (1) the addition of low melting point compounds or glass-forming additives to reduce the sintering temperature of commercially developed dielectric ceramics, however, in many cases, the additions produce a significant deterioration in $Q \times f$ values, (2) the chemical processing and smaller particle size of starting materials by the sol-gel and coprecipitation methods, and (3) a study of new series of dielectric ceramics with low sintering temperature such as $BiNbO_4$, TiO_2–TeO_2, and $ZnTiO_3$ [1,9]. Recently, many studies have been focused on Li-containing compounds which have low sintering temperature and excellent microwave dielectric properties, such as $Li_{1+x-y}Nb_{1-3x-3y}Ti_{x+4y}O_3$ ($x = 0.1$, $y = 0.05$–0.175) ceramics [10–12], Li_3NbO_4 [13], $Ca(Li_{1/3}Nb_{2/3})O_3$ [7,14], $Li_{0.5}Sm_{0.5}WO_4$ [8], $Ba_4LiNb_{3-x}Ta_xO_{12}$ ($x = 0$–3) [15] and Li_2MgSiO_4 [16]. More recently, the microwave dielectric properties of two cubic spinels $Li_2ATi_3O_8$ (A = Zn, Mg) are reported by Zhou et al. [17] and Sebastian et al. [18], respectively. These ceramics are well sintered below 1100 °C, and exhibit good microwave dielectric properties with ε_r in the range 25.6–27.5, $Q \times f$ up to 72,000 GHz and low τ_f in the range −15–3.2 ppm/°C. Furthermore, these materials are advantageous in terms of low cost production (low cost of raw materials and low sintering temperature) and low bulk density (for lightness of the electronic module) compared to commercially available ceramics such as BMT and ZST.

Since the Shannon's effective ionic radii of Co^{2+} (0.745 Å) are very similar to those of Mg^{2+}(0.72 Å) and Zn^{2+}(0.74 Å) [19], and

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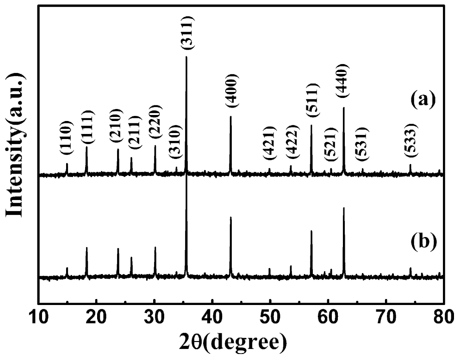

Fig. 1. X-ray diffraction patterns of (a) $Li_2CoTi_3O_8$ power calcined at 900 °C for 4 h, and (b) $Li_2CoTi_3O_8$ ceramics sintered at 1025 °C for 2 h.

Co substitutions for Mg in the $Mg_3(VO_4)_2$ ceramics has been reported to effectively lower the sintering temperature [20], then it is worthwhile to investigate whether $Li_2CoTi_3O_8$ ceramic might exhibit equivalent or superior properties. The crystal chemistry and physical properties of $Li_2CoTi_3O_8$ ceramic were reported by Kawai et al. [21], however, the microwave dielectric properties of $Li_2CoTi_3O_8$ ceramic have not been reported as yet. In present study, the microwave dielectric properties, phase structure and microstructure of $Li_2CoTi_3O_8$ are investigated. Since BCB is generally chosen as a candidate sintering aid due to its low melting point (850 °C), and the favorable microwave dielectric properties ($\varepsilon_r \sim 7.4$, $Q \times f \sim 50{,}000$ GHz, $\tau_f \sim -32$ ppm/°C) [22], which was successfully applied in lowering the sintering temperatures of several ceramics such as $Ba(Zn_{1/3}Nb_{2/3})O_3$, $ZnO–2TiO_2–Nb_2O_5$ and $Ba_4LiNb_3O_{12}$ ceramics [23–25]. Then, the low temperature sintering behavior of $Li_2CoTi_3O_8$ ceramic with the addition of BCB is also reported.

2. Experimental procedures

Specimens of the $Li_2CoTi_3O_8$ ceramics were prepared by a conventional mixed oxide route from the high-purity oxide powders of Li_2CO_3 (≥99.9%), Co_2O_3 (≥99%) and TiO_2 (≥99.9%). Stoichiometric proportions of the above raw materials were weighed and milled in alcohol medium using zirconia balls for 4 h. The mixtures were dried and calcined at 900 °C for 4 h with a heating rate of 5 °C/min. To synthesize the BCB ceramic powder, $BaCO_3$ (99.9%), CuO (99.9%) and B_2O_3 (99.9%) were mixed for 4 h in a nylon jar with zirconia balls, then dried and calcined at 700 °C for 4 h with a heating rate of 5 °C/min. With subsequent ball-milling with 0.5–2.0 wt% BCB, the powders were uniaxially pressed under the pressure of about 150 MPa into disks of 12 mm in diameter and 6–7 mm in thickness. The pure samples were sintered in the temperature range of 975–1075 °C for 2 h and the ceramic pellets doped with BCB were sintered at 850–950 °C for 2 h in air. The heating rate of the sintering process is 5 °C/min.

The crystal structures of the specimens were analyzed by an X-ray diffractometer (X'Pert PRO, PANalytical, Almelo, Holland) with Cu K_α radiation generated at 40 kV and 100 mA. The bulk densities of the sintered samples were measured by the Archimedes method. The microstructure observation of the samples was performed using scanning electron microscopy (JSM6380-LV, JEOL, Tokyo, Japan).

The microwave dielectric properties were obtained using a network analyzer (Model N5230A, Agilent Co., Palo Alto, Canada) and a temperature chamber (Delta 9039, Delta Design, San Diego, CA). The temperature coefficients of resonant frequency τ_f values were calculated by the formula as following:

$$\tau_f = \frac{f_T - f_0}{f_0(T - T_0)} \tag{1}$$

where f_T, f_0 were the resonant frequencies at the measuring temperature T (85 °C) and T_0 (25 °C), respectively.

3. Results and discussion

The room-temperature X-ray diffraction patterns recorded for $Li_2CoTi_3O_8$ powders calcined at 900 °C and the ceramic sintered at 1025 °C using CuK_α radiation are shown in Fig. 1(a) and 1(b), respectively. All the peaks are indexed based on the PDF files No. 00-049-0449 with a $P4_332$ (2 1 2) cubic cell, $a = 8.3766(12)$ Å, $V = 587.49$ Å^3, and $Z = 4$ (Z denotes the number of molecules in the unit cell), which agrees well with that reported by Kawai et al. [21], and no additional peaks is observed, implying that $Li_2CoTi_3O_8$ formed in the single cubic spinel phase. Therefore, it is considered that the phase pure $Li_2CoTi_3O_8$ could be obtained when the calcining temperature is 900 °C (as shown in Fig. 1(a)). Besides, it is reported that in the spinel structure Co shows strong preference for tetrahedral sites, and 1: 3 cation ordering of Li/Co and Ti occurs on the octahedral sites [21].

The microstructures of the $Li_2CoTi_3O_8$ ceramics sintered at various temperatures investigated using SEM are shown in Fig. 2. For the specimen sintered at 975 °C, the microstructure is observed with several pores, and most of the grain sizes are small, approx-

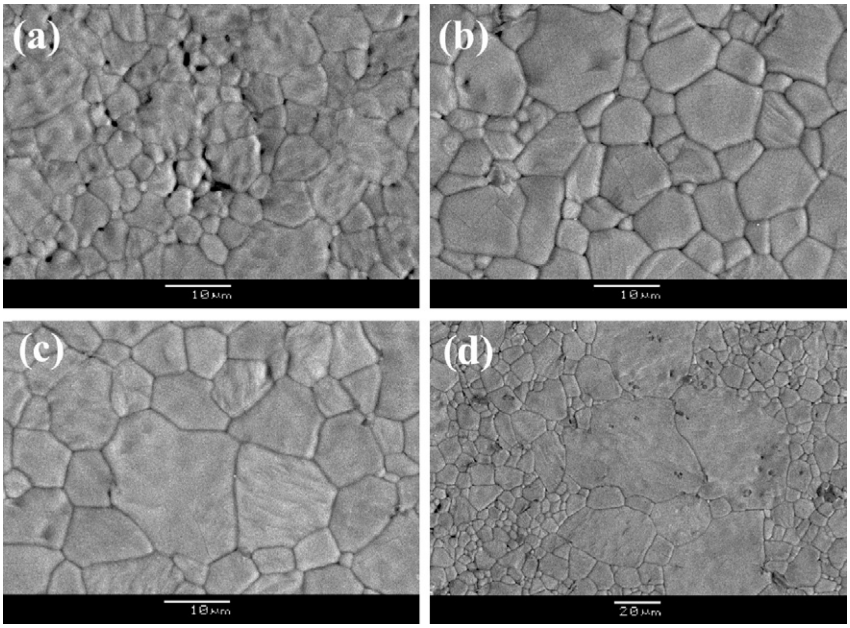

Fig. 2. Scanning electron micrographs of the $Li_2CoTi_3O_8$ ceramics sintered at various temperatures: (a) 975 °C, (b) 1000 °C, (c) 1025 °C, and (d) 1050 °C.

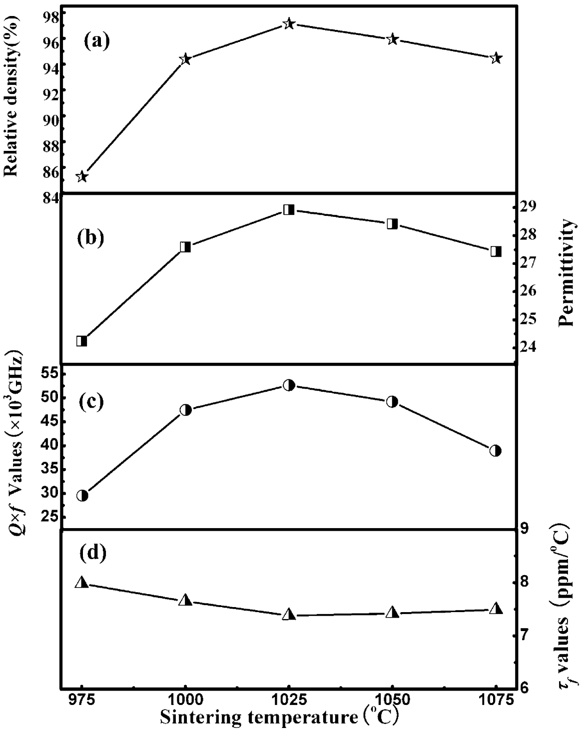

Fig. 3. The variation of (a) relative densities, (b) relative permittivity, (c) quality factor, and (d) temperature coefficient of the resonant frequency of $Li_2CoTi_3O_8$ ceramics as a function of sintering temperature.

imately 5 μm. When the sintering temperature increases from 1000 °C to 1025 °C, the grains growth is observed and dense microstructure with the closely packed grains are developed, as shown in Fig. 2(b) and (c). The majority of the grains are in the size of 6–15 μm. However, as the sintering temperature exceeds 1025 °C, abnormal grain growth occurs, and a few large grains with an average size of 40–50 μm and a small amount of trapped porosity at the grain boundaries caused by the evaporation of lithium and the decrease of the grain boundary area are observed, as shown in Fig. 2(d).

The relative densities and the microwave dielectric properties of $Li_2CoTi_3O_8$ ceramics as a function of the sintering temperature are illustrated in Fig. 3. As the sintering temperature increases from 975 to 1025 °C, the bulk density increases from 3.32 to 3.78 g/cm^3, which is equivalent to a relative density of about 97.1%. When the sintering temperature further increases, the density of $Li_2CoTi_3O_8$ ceramics reaches saturation. Fig. 3(b)–(d) shows the ε_r, $Q \times f$, and τ_f values of the $Li_2CoTi_3O_8$ ceramics sintered at various temperatures, respectively. The ε_r value is considerable low for the specimen sintered at 975 °C, probably due to the low density, and it increases considerably from 24.2 to 28.9 with increasing temperature, then decreases slightly as the sintering temperature is over 1025, which may be related to small amount of trapped porosity and the abnormal grain growth caused by the decrease of the grain boundary area. The variation trend between ε_r and sintering temperatures is similar to bulk densities and sintering temperatures. Due to the increased densities, the $Q \times f$ values first increase with the increase in sintering temperature and exhibit a maximum value of 52,600 GHz (at 6.34 GHz) for the specimen sintered at 1025 °C. Thereafter, the $Q \times f$ values decrease with further increasing temperature, which may be due to extrinsic factors, such as the increase in liquid phase, and the grain abnormal growth [18]. Moreover, Sebastian et al. [1,16,18] reported that the volatile Li has a deleterious effect on dielectric properties, which attributes to the deficiency of Li leads to decrease in density and lattice defects. The τ_f values do not change remarkably with increasing sintering temperature and remain stable around 7.4 ppm/°C.

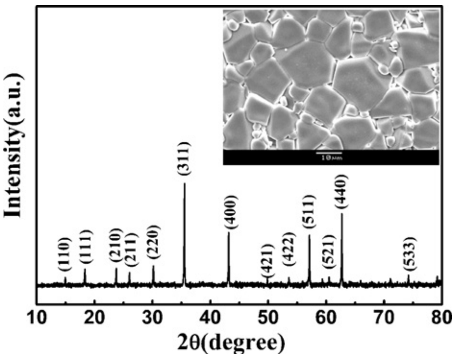

Fig. 4. XRD patterns of 1.5 wt% BCB-added $Li_2CoTi_3O_8$ ceramics sintered at 900 °C for 2 h. Insert shows scanning electron micrographs of the $Li_2CoTi_3O_8$ samples doped with 1.5 wt% BCB sintered at 900 °C for 2 h.

The microwave dielectric properties of $Li_2MTi_3O_8$ (M = Co, Mg, Zn) ceramics are summarized in Table 1 [18]. It is clear that the optimized sintering temperature of the $Li_2CoTi_3O_8$ ceramic (at 1025 °C) is 50 °C lower than those of $Li_2ATi_3O_8$ (A = Zn, Mg) ceramics [18]. The ε_r of $Li_2CoTi_3O_8$ ceramic is slightly higher than those of $Li_2ATi_3O_8$ (A = Zn, Mg) ceramics, which may attribute to higher relative density since their average ionic polarizability ($\alpha^T{}_D/V_m$, where $\alpha^T{}_D$ is the sum of ionic polarizability of individual ions, and V_m is the molar volume) are near the same(~0.19) calculated from modified Clausius–Mossotti equation [1,25]. The $Q \times f$ and τ_f values are between those of the $Li_2MgTi_3O_8$ and $Li_2ZnTi_3O_8$ ceramics.

Compared with other glasses added to reduce the sintering temperature of the materials, BCB not only has a low melting point (~850 °C), but also exhibits favorable microwave dielectric properties ($\varepsilon_r \sim 7.4$, $Q \times f \sim 50{,}000$ GHz, $\tau_f \sim -32$ ppm/°C). To further decrease the sintering temperature of the ceramic to cofire with Ag electrode, a small amount of BCB has been doped into the samples. Due to the liquid phase presence, the addition of BCB can efficiently lower the sintering temperature of $Li_2CoTi_3O_8$ ceramic from 1025 °C to 900 °C. The average grain size of 1.5 wt% BCB-added ceramics (6–18 μm) is similar to that of the pure ceramic, as shown in Fig. 4 (Insert). The XRD patterns of the 2 wt% BCB-added ceramics sintered at 900 °C are well matched with PDF files No. 00-049-0449, and no secondary phase could be detected, as shown in Fig. 4. The relative densities of the samples increase with increasing the sintering temperatures from 850 °C to 900 °C, and saturate at the sintering temperatures higher than 900 °C, approximately 95%. The variations in the permittivity show the similar tendency to those of relative density. The $Q \times f$ values of the $Li_2CoTi_3O_8$ ceramic significantly increase with increasing BCB content and sintering

Table 1
Sintering temperatures, relative densities, and microwave dielectric properties of $Li_2MTi_3O_8$ (M = Mg, Co, Zn) ceramics.

M	Relative density (%)	$\alpha^T{}_D/V_m$	Sintering temperature (°C)	ε_r	Q × f (GHz)	τ_f (ppm/°C)	Ref.
Co	97.1	0.1969	1025	28.9	52,600	7.4	–
Mg	95.5	0.1945	1075	27.2	42,000	3.2	[18]
Zn	95	0.1999	1075	25.6	72,000	−11.2	[18]

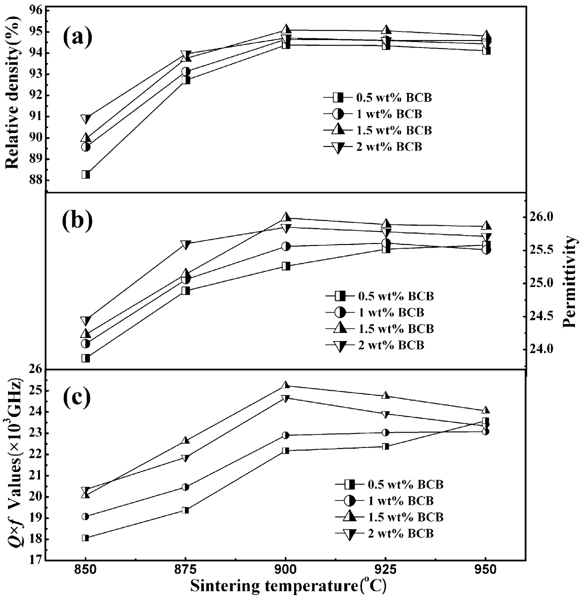

Fig. 5. The variation of (a) relative densities, (b) relative permittivity, and (c) quality factor of $Li_2CoTi_3O_8$ ceramics doped with 0.5–2 wt% BCB as a function of sintering temperature.

temperature, and the maximum $Q\times f$ value is obtained with 1.5 wt% BCB at 900 °C (as shown in Fig. 5). Owing to BCB exhibiting negative τ_f value, the τ_f values significantly decrease with the addition of BCB (as shown in Fig. 6). For the BCB-added ceramic, a high relative density of 95% and better microwave dielectric properties of $\varepsilon_r = 26.0$, $Q\times f = 25{,}200$ GHz, $\tau_f = -6.8$ ppm/°C have been obtained by sintering at 900 °C.

In order to evaluate the chemical compatibility of $Li_2CoTi_3O_8$ ceramic with silver electrode, the mixtures of 1.5 wt% BCB added $Li_2CoTi_3O_8$ powders and 20 wt% Ag powders are cofired at 900 °C for 2 h in air and analyzed to detect interactions between the low-fired samples and electrodes. The X-ray powder diffraction pattern (XRPD) and a backscattered electron image of $Li_2CoTi_3O_8$ ceramic added with 1.5 wt% BCB cofired with Ag at 900 °C are also shown in Fig. 7. Since the XRPD pattern of the mixtures does not show the formation of other phase and the backscattered electron image of 1.5 wt% BCB added $Li_2CoTi_3O_8$/Ag sample cofired at 875 °C for 2 h reveals no interaction to form new phases after firing, it is considered that the $Li_2CoTi_3O_8$ ceramic with 1.5 wt% BCB additives has a chemical compatibility with silver electrodes.

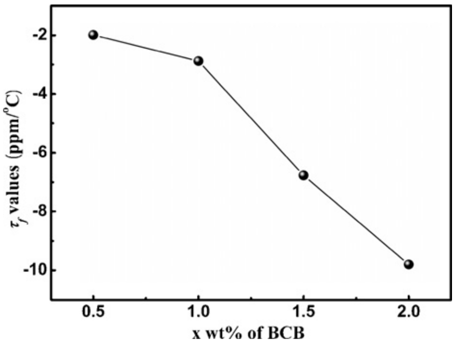

Fig. 6. Variations of the τ_f values of the $Li_2CoTi_3O_8$ ceramics containing x wt% of BCB with $0.5 \le x \le 2$ sintered at 900 °C for 2 h.

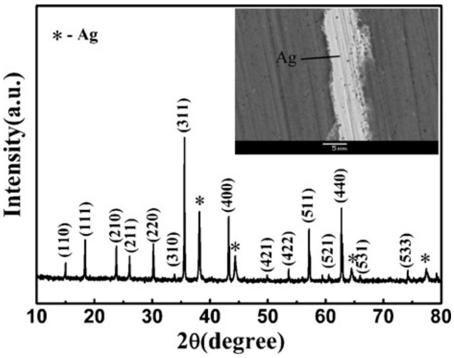

Fig. 7. XRD patterns of 1.5 wt% BCB-added $Li_2CoTi_3O_8$ ceramics mixed with 20 wt% Ag sintered at 900 °C for 2 h. Insert shows a backscattered electron image of 1.5 wt% BCB-added $Li_2CoTi_3O_8$ samples cofired with Ag.

4. Conclusions

A Li-containing microwave dielectric ceramic $Li_2CoTi_3O_8$ with cubic spinel structure has been synthesized by the conventional solid-state ceramic route. This new material sintered at 1025 °C for 2 h exhibits a moderate dielectric constant (ε_r) of 28.9, a high quality factor value ($Q\times f$) of 52,600 GHz, and a low temperature coefficient of the resonant frequency (τ_f) of 7.4 ppm/°C. This ceramic shows a good combination of low bulk density, low cost of raw materials, low sintering temperature, and good microwave dielectric properties, and the addition of 1.5 wt% BCB can reduce the sintering temperature to 900 °C and induce only a limited degradation of the microwave dielectric properties ($\varepsilon_r = 26.0$, $Q\times f = 25{,}200$ GHz, $\tau_f = -6.8$ ppm/°C). It is important that $Li_2CoTi_3O_8$ ceramic with 1.5 wt% BCB additives has a chemical compatibility with silver, which might be an attractive promising candidate for LTCC application.

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References

[1] T. Sebastian, Dielectric Materials for Wireless Communications, Elseiver Publishers, Oxford, UK, 2008.
[2] C.H. Shen, C.L. Huang, L.M. Lin, C.L. Pan, J. Alloys Compd. 489 (2010) 170.
[3] P.S. Anjana, T. Joseph, M.T. Sebastian, J. Alloys Compd. 490 (2010) 208.
[4] H. Zhang, Y. Wu, S. Meng, L. Fang, J. Alloys Compd. 460 (2008) 460.
[5] C. Li, L. Fang, X. Peng, C. Hu, B. Wu, J. Alloys Compd. 500 (2010) L9.
[6] C.Z. Hu, L. Fang, H.P. Su, L.J. Liu, B.L. Wu, J. Alloys Compd. 487 (2009) 504.
[7] S. George, M.T. Sebastian, J. Alloys Compd. 473 (2009) 336.
[8] H. Yang, Y. Lin, J. Zhu, F. Wang, Z. Dai, J. Alloys Compd. 502 (2010) L20.
[9] M.T. Sebastian, H. Jantunen, Int. Mater. Rev. 53 (2008) 57.
[10] A. Borosevich, P.K. Davies, J. Eur. Ceram. Soc. 21 (2000) 1719.
[11] A. Borisevich, P.K. Davies, J. Am. Ceram. Soc. 85 (2002) 2487.
[12] H.F. Zhou, H. Wang, D. Zhou, L.X. Pang, X. Yao, Mater. Chem. Phys. 109 (2008) 510.
[13] D. Zhou, H. Wang, L.X. Pang, X. Yao, X.G. Wu, J. Am. Ceram. Soc. 91 (2008) 4115.
[14] P. Liu, E.S. Kim, K.H. Yoon, Jpn. J. Appl. Phys. 40 (2001) 5769.
[15] L. Fang, C.C. Li, X.Y. Peng, C.Z. Hu, B.L. Wu, H.F. Zhou, J. Am. Ceram. Soc. 93 (2010) 1229.
[16] S. George, P.S. Anjana, V.N. Deepu, P. Mohanan, M.T. Sebastian, J. Am. Ceram. Soc. 92 (2009) 1244.
[17] H.F. Zhou, X.L. Chen, L. Fang, D.J. Chu, H. Wang, J. Mater. Res. 25 (2010) 1235.
[18] S. George, M.T. Sebastian, J. Am. Ceram. Soc. 93 (2010) 2164.
[19] R.D. Shannon, J. Appl. Phys. 73 (1993) 348.

[20] R. Umemura, H. Ogawa, H. Ohsato, A. Kan, A. Yokoi, J. Eur. Ceram. Soc. 25 (2005) 2865.
[21] H. Kawai, M. Tabuchi, M. Nagata, H. Tukamoto, A.R. West, J. Mater. Chem. 8 (1998) 1273.
[22] M.H. Kim, J.B. Lim, J.C. Kim, S. Nahm, J.H. Paik, J.H. Kim, K.S. Park, J. Am. Ceram. Soc. 89 (2006) 3124.
[23] H.F. Zhou, H. Wang, K.C. Li, H.B. Yang, M.H. Zhang, X. Yao, J. Electron. Mater. 38 (2009) 711.
[24] L. Fang, D.J. Chu, C.C. Li, H.F. Zhou, Z. Yang, J. Am. Ceram. Soc. (2010), doi:10.1111/j.1551-2916.2010.04100.x.
[25] L. Fang, C.C. Li, X.Y. Peng, C.Z. Hu, B.L. Wu, J. Am. Ceram. Soc. 93 (2010) 1884.