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Low-temperature sintering and dielectric properties of the $Bi(Nb_{1-x}Ta_x)O_4$ system

Dae Min Kim · Shin Kim · Kwan Soo Kim · Sang Ok Yoon · Jong Guk Park

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Abstract Low-temperature sintering and dielectric properties of the $Bi(Nb_{1-x}Ta_x)O_4$ (x=0.1, 0.3, and 0.5) system was investigated as a function of the zinc borosilicate (ZBS) glass content with a view to applying this system to LTCC technology. The addition of 7 wt% ZBS glass ensured a successful sintering below 900°C. The complete solid solution of Bi(Nb, Ta)O_4 with an orthorhombic structure was formed and the high temperature form of Bi(Nb, Ta)O_4 with a triclinic structure was not observed. The second phase of Bi_2SiO_5 was observed for all compositions. The non-relative liquid phase sintering (NLPS) occurred and the one-stage sintering was conducted. The $Q\times f$ values were improved by the addition of Ta. $Bi(Nb_{0.7}Ta_{0.3})O_4$ with 7 wt% ZBS glass sintered at 900°C demonstrated 35.8 in the dielectric constant (ε_r), 2,200 GHz in the quality factor ($Q\times f_0$), and −48 ppm/°C in the temperature coefficient of resonant frequency (τ_f).

Keywords $BiNbO_4$ · $Bi(Nb_{1-x}Ta_x)O_4$ · LTCC · Zinc-borosilicate · Dielectrics

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1 Introduction

Multilayer microwave devices are becoming increasingly important with the rapid progress of miniaturization in mobile communication systems [1]. In order to satisfy the devices requirement, the microwave dielectric ceramics with low sintering temperature are needed to co-fire with low loss conductors such as Ag or Cu. The sintering temperatures of conventional microwave dielectric ceramics are too high to use the low melting point and low cost electrodes [2–4]. Low melting glass additions, chemical processing, and smaller particle sizes of the starting materials are three methods normally used to reduce the sintering temperature of dielectric materials [5–8].

Bismuth-based dielectric ceramics are well known as low-firing materials and have been studied for multilayer capacitors. Since Kagata et al. [9] reported the microwave dielectric properties of $BiNbO_4$ (ε_r=43, $Q\times f$ values= 10,000~17,000 GHz) with sintering aids, various attempts have been undertaken to improve the microwave dielectric properties of $BiNbO_4$, such as the substitution of lanthanide for Bi, the solid solutions of $Bi(Nb_{1-x}Ta_x)O_4$, $Bi(Nb_{1-x}Sb_x)O_4$ and the addition of various sintering aids. Also, the ABO_4 ($A=Bi^{3+}$, Sb^{3+}, $B=Nb^{5+}$, Ta^{5+}, Sb^{5+}) compounds with stibiotantalite structure are known to exhibit multiple structural and dielectric phase transitions [9–11]. $BiTaO_4$ ceramics have a similar crystal structure with $BiNbO_4$ ceramics and its dielectric properties at microwave frequency were studied by Huang and Weng [10]. $BiTaO_4$ ceramics with 0.5 wt% CuO addition exhibited high $Q\times f$ values (8,000~12,000 GHz) and a negative τ_f value (−40 ppm/°C). Its dielectric constant saturated at 43~44. The effects of Ta substitution for Nb on sintering behavior and microwave dielectric properties of $BiNbO_4$ ceramics were studied by Wang et al. [11]. The

$BiNb_{0.9}Ta_{0.1}O_4$ ceramics sintered at 820°C exhibited the best microwave dielectric properties of ε_r=44.35, $Q\times f$ value=3,850 GHz, and τ_f=0.52 ppm/°C. However, only $Bi(Nb_{1-x}Ta_x)O_4$ solid solution or sintering aids added $Bi(Nb_{1-x}Ta_x)O_4$ were reported. In this study, the sintering and microwave dielectric properties of zinc-borosilicate glass (hereafter ZBS glass) added $Bi(Nb_{1-x}Ta_x)O_4$ (x=0.1, 0.3 and 0.5) system with were investigated in the view point of the application to LTCC materials.

2 Experimental procedure

To prepare $Bi(Nb_{1-x}Ta_x)O_4$ (x=0.1, 0.3 and 0.5) power (denotes as BNTx), the proper ratio of Bi_2O_3, Nb_2O_5, and Ta_2O_5 powders (purity 99.9%) were ball-milled for 24 hr and then calcined at 800°C for 3 hr. The powders of ZnO, B_2O_3 and SiO_2 with a grade of extra-pure reagent were well mixed and the ZBS glass frit was obtained by a quenching method after a melting process at 1300°C. The deformation temperature of the ZBS glass was measured by a dilatometer (DIL 402, Netzsch). The BNTx–ZBS system composed of 3~10 wt% glass was ball-milled for 24 hr and then dried. The disk type specimens with a 15 mm in diameter were prepared by a pressing of powder mixtures under 1,500 kg/cm^2 and sintering processes at between 825~925°C with an interval of 25°C for 2 hr. The phase analysis was carried out by an X-ray diffractometer (D/Max-2200, Rigaku, Japan) using a Cu-Kα target and a Ni filter with 2theta range of 10~80. The microstructures were observed by a FE-SEM (S-4200, Hitachi). The dielectric constant (ε_r) and the $Q\times f$ value were measured by Hakki-Coleman method using a network analyzer (HP8720ES) and specimens which were placed between two parallel metal plates; the resonant frequency, the half power bandwidth which was recorded at 3dB level of the resonant peak, and the insertion loss were measured [12]. The temperature coefficient of resonant frequency (τ_f) was measured using an invar cavity in the temperature range of between 25 and 85°C.

Table 1 Density, deformation temperature and dielectric properties of ZBS glasses.

	ZBS glass	Zn60B30Si10
Density (g/cm^3)	3.57	3.60[a]
Deformation point (°C)	588	582
Dielectric constant, (ε_r)	6.53	7.56
Resonant frequency (GHz)	17.1	15.5
Q	261	93
$Q\times f_0$ (GHz)	4,465	1,439
τ_f (ppm/°C)	−10	−21
Remarks	This work	[13]

[a] [14]

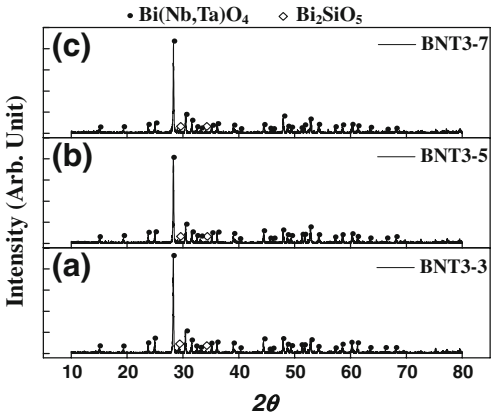

Fig. 1 XRD patterns of the $Bi(Nb_{0.7}Ta_{0.3})O_4$–ZBS system sintered at 900°C; (**a**) 3 wt%, (**b**) 5 wt%, and (**c**) 7 wt% ZBS glass

3 Results and discussion

3.1 ZBS glass-doped $Bi(Nb_{0.7}Ta_{0.3})O_4$ ceramics

The deformation temperature of the ZBS glass, i.e., the temperature at the maximum value of thermal expansion curve, was determined as 588°C, which was similar with the value in the literature; it of zinc borosilicate glass with the composition of $60ZnO\text{-}30B_2O_3\text{-}10SiO_2$ (in mol%, Zn60B30Si10) was reported as 582°C by Wu et al. [13]. They also determined the dielectric constant (ε_r), the $Q\times f$ value, and the temperature coefficient of resonant frequency (τ_f) of this glass as 7.56, 1 439 GHz (93 at 15.5 Hz), and −21 ppm/°C, respectively. Density, deformation point and dielectric properties of the ZBS glasses were summarized in Table 1 and these glasses showed similar properties except $Q\times f$ value and τ_f.

The XRD patterns of the $Bi(Nb_{0.7}Ta_{0.3})O_4$–ZBS system containing 3, 5, and 7 wt% ZBS glass (6.4, 10.4, and 14.3 vol., respectively) sintered at 900°C were shown in Fig. 1; (a) $Bi(Nb_{0.7}Ta_{0.3})O_4$–3 wt% ZBS glass (denoted as BNT3-3) and (b) 5 wt% ZBS glass (BNT3-5), and (c) 7 wt%

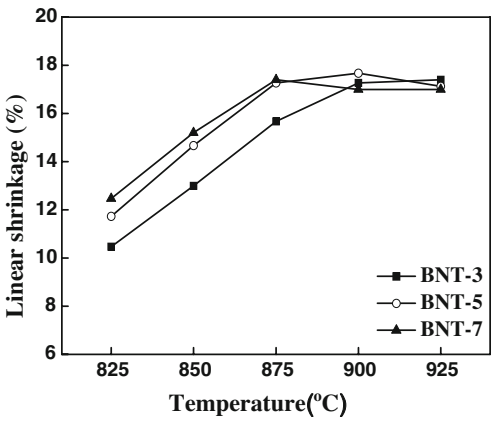

Fig. 2 Linear shrinkage of the $Bi(Nb_{0.7}Ta_{0.3})O_4$–ZBS system as a function of the sintering temperature

ZBS glass (BNT3-7). All compositions showed Bi(Nb, Ta)O_4 of an orthorhombic structure as the main crystalline phase with the minor phase of Bi_2SiO_5 of a tetragonal structure. $BiNbO_4$ and $BiTaO_4$ had two polymorphs of the low-temperature orthorhombic structure and the high-temperature triclinic structure and their irreversible phase-transition temperature was 1005°C and 725°C, respectively [15]. However, the triclinic structure was not obtained in this work when the sintering process conducted at 900°C. The

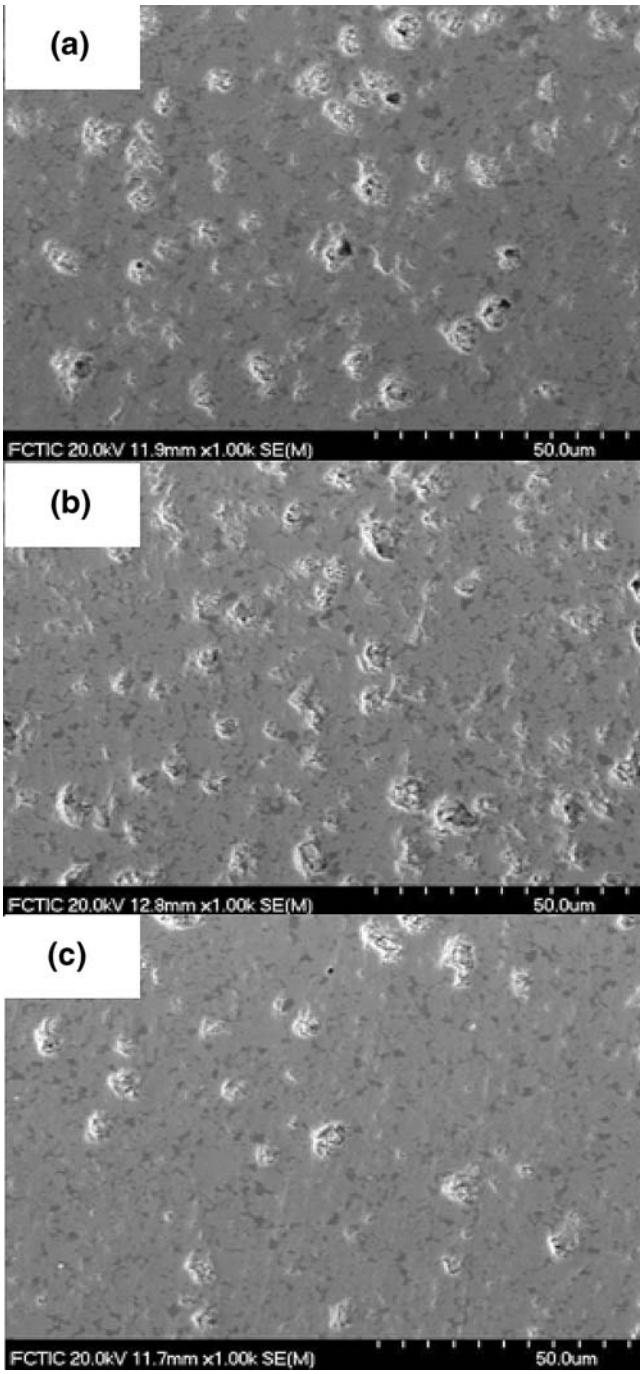

Fig. 3 Microstructures of the $Bi(Nb_{0.7}Ta_{0.3})O_4$–ZBS system sintered at 900°C; (**a**) 3 wt%, (**b**) 5 wt% and (**c**) 7 wt% ZBS glass

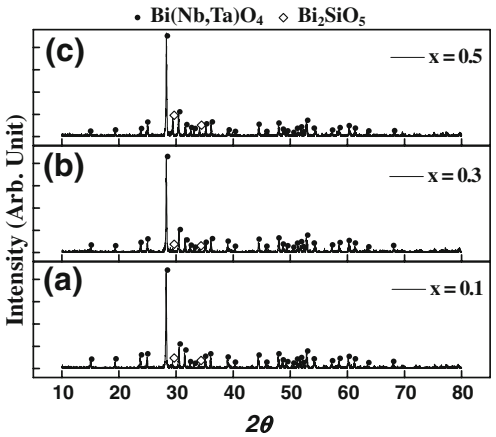

Fig. 4 XRD patterns of the $Bi(Nb_{1-x}Ta_x)O_4$–7 wt% ZBS glass system sintered at 900°C; (**a**) x=0.1, (**b**) x=0.3, and (**c**) x=0.5

formation of Bi_2SiO_5, on the other hand, indicated that the reaction between Bi(Nb, Ta)O_4 and silicon in the ZBS glass occurred. And it was reported by Georges et al. that Bi_2SiO_5 also had two polymorphs of the low-temperature orthorhombic structure and the high-temperature tetragonal structure [16]. They also stated that the tetragonal form was stabilized by partial substitution of Bi^{3+} by La^{3+}. From the result that the high-temperature form was maintained at room temperature in this work, it is considered that Bi in Bi_2SiO_5 might be substituted by Zn^{2+} in the ZBS glass and the stabilization of the high-temperature form resulted in.

The linear shrinkage behavior of the compositions for BNT-3, BNT-5, and BNT-7 as a function of the sintering temperature was shown in Fig. 2. It is understandable that all specimens having 6.4~14.3 vol.% ZBS glass were sufficiently sintered under 900°C. But for the specimen with 10 wt% ZBS glass, the reaction between the specimen and the ceramic substrates during the sintering occurred. From the facts that the deformation temperature of the ZBS glass was 588°C and there was no reaction between Bi(Nb, Ta)O_4 and the ZBS glass although a small amount of Bi_2SiO_5 was crystallize, the sintering behavior could be interpreted as the one-stage sintering. It is, moreover, considered that the non-reactive liquid phase sintering (NPLS) occurred in this system [17, 18]. The NLPS is one of the liquid-assisted sintering (LAS) [19]; LAS distinguishes between the NLPS, where a glass phase content of at least 20–40 vol.% is necessary for the densification and a reactive liquid phase sintering, where a glass content <20 vol.% is sufficient. The densification in the NLPS was proposed in three stages; the first stage is glass redistribution and local grain rearrangement where only slight densification occurs, the second is the main densification process including global rearrangement, glass redistribution, and closure of pores where the density from 65 to 90% of the theoretical density is accomplished, and the third is viscous flow where the residual porosity of

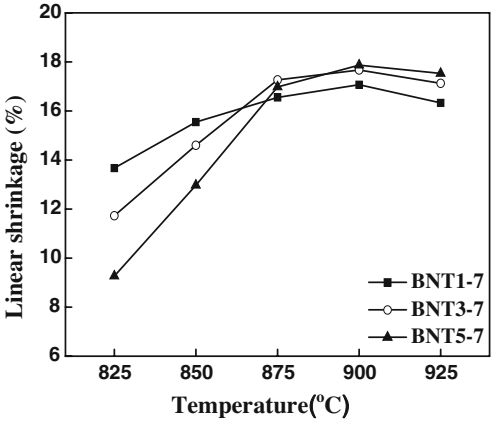

Fig. 5 Linear shrinkage of the $Bi(Nb_{1-x}Ta_x)O_4$–7 wt% ZBS glass system as a function of the sintering temperature

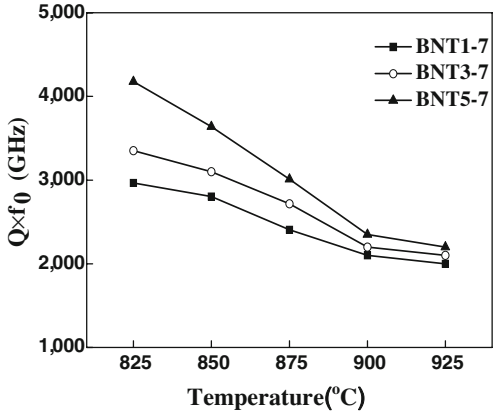

Fig. 7 $Q \times f$ values of the $Bi(Nb_{1-x}Ta_x)O_4$–7 wt% ZBS glass system as a function of the sintering temperature

about 10% is closed. The behavior of the linear shrinkage against the sintering temperature was expected as an S-type curve. Figure 3 shows the microstructures of BNT-3, BNT-5, and BNT-7 which were sintered at 900°C. It is understandable that the amount of the closed pore decreased as the increase of the ZBS glass contents, indicating that the liquid phase promoted the densification and then the pore filling resulted in. Further investigation in this work, therefore, was conducted for 7 wt% ZBS glass added compositions although some closed pores still existed.

3.2 7 wt% ZBS glass-doped $Bi(Nb_{1-x}Ta_x)O_4$ ceramics

The XRD patterns of the $Bi(Nb_{1-x}Ta_x)O_4$–7 wt% ZBS system sintered at 900°C were shown in Fig. 4; (a) x=0.1, $Bi(Nb_{0.7}Ta_{0.3})O_4$–7 wt% ZBS glass (BNT1-7), (b) x=0.3, (BNT3-7), and x=0.5, (BNT5-7). In all compositions, the crystalline phases of the Bi(Nb, Ta)O_4 solid solution and Bi_2SiO_5 as the second phase were observed, which was similar to Fig. 1. Since the ionic radii of Ta^{5+} and Nb^{5+} are same as 0.064 nm (C.N.=6) [20], $BiNbO_4$ and $BiTaO_4$ would form a complete solid solution where Nb and Ta might randomly exist in the cation sub-lattice. The linear shrinkage behavior of the compositions for BNT1-7, BNT3-7, and BNT5-7 as a function of the sintering temperature was shown in Fig. 5. In the low temperature region, the linear shrinkage decreased as the amount of Ta increased. The similar result was reported in the $BiNb_{(1-x)}Ta_xO_4$ (x=0~0.4) system and the higher sintering temperature of $BiTaO_4$ than that of $BiNbO_4$ was suggested as the reason of this phenomenon [21].

The dielectric constant (ε_r) of BNT1-7, BNT3-7, and BNT5-7 as a function of the sintering temperature was shown in Fig. 6. As the sintering temperature increased, the dielectric constant increased, implying that the dielectric constant might be affected by the densification because the behavior of the dielectric constant against the temperature was similar with that of the linear shrinkage as shown in Fig. 5. Generally, the dielectric constant often exhibited the same trend with the density since dense ceramics had less pores (air, ε_r=1) which decayed the ε_r value of the dielectrics. The $Q \times f$ values of BNT1-7, BNT3-7, and BNT5-7 as a function of the sintering temperature was

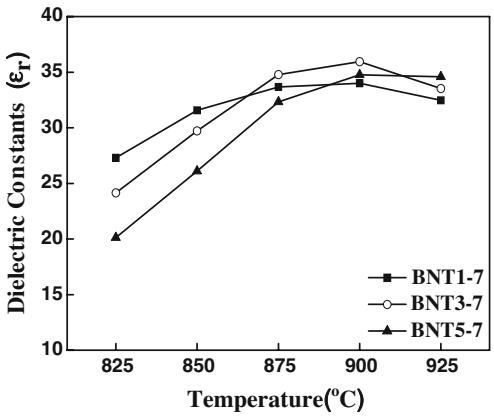

Fig. 6 Dielectric constant of the $Bi(Nb_{1-x}Ta_x)O_4$–7 wt% ZBS glass system as a function of the sintering temperature

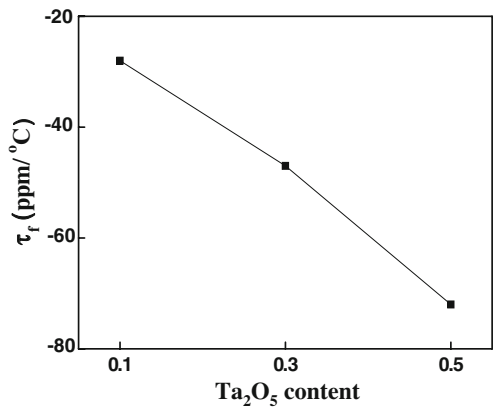

Fig. 8 Temperature coefficient of resonant frequency of the $Bi(Nb_{1-x}Ta_x)O_4$–7 wt% ZBS glass system sintered at 900°C

shown in Fig. 7. Within the low temperature region, the higher value of $Q\times f$ was obtained as the amount of Ta increased although the lower linear shrinkage was observed as shown in Fig. 5, implying that by doping of Ta might improve the $Q\times f$. The increase of the $Q\times f$ value with the increase of Ta content from 0 to 0.6 in the $BiNb_{(1-x)}Ta_xO_4$ system was also reported [21]. On the other hand, the $Q\times f$ value decreased as the sintering temperature increased in all compositions. It is suggested that the substitution of zinc in the ZBS glass on Bi-site and the subsequent oxygen-vacancy formation for the charge compensation might occur and then the decrease of the $Q\times f$ value resulted in. As the higher sintering temperature increased, the substitution might be promoted and the amount of oxygen vacancy might be increased. The relatively low $Q\times f$ values under 5,000 GHz in this work supports this suggestion. For a material having high quality factor and low dielectric loss, it is necessary to reduce the attenuation constant; it is known that the anharmonicity in the lattice vibration affects the attenuation constant for perfect crystals (i.e., intrinsic loss) whereas dislocations, pores, defects, grain boundaries, and secondary phases have an influence on the attenuation constant for poly-crystals (i.e., extrinsic loss) [22, 23]. In general, the amounts of pores and grain boundaries decrease with increasing of the density and then dielectric losses are reduced. Figure 8 shows the temperature coefficient of the resonant frequency (τ_f) of $Bi(Nb_{1-x}Ta_x)O_4$–7 wt% ZBS systems when the sintering was conducted at 900°C. The value decreased with the increase of x, i.e., Ta content, and varied from −30 to −70 ppm/°C and the similar results were also reported [25]. BNT3-7, i.e., $Bi(Nb_{0.7}Ta_{0.3})O_4$ with 7 wt% ZBS glass, sintered at 900°C demonstrated 35.8 in the dielectric constant (ε_r), 2,200 GHz in the $Q\times f$ value, and −48 ppm/°C in the temperature coefficient of resonant frequency (τ_f).

4 Conclusions

Low-temperature sintering and microwave dielectric properties of the $Bi(Nb_{1-x}Ta_x)O_4$ (x=0.1, 0.3 and 0.5)–ZBS glass system was investigated. The addition of 7 wt% ZBS glass ensured successful sintering below 900°C. But for the specimen with 10 wt% ZBS glass, the reaction between the specimen and the ceramic substrates during the sintering occurred. From the facts that the deformation temperature of the ZBS glass was 588°C and there was no reaction between Bi(Nb, Ta)O_4 and the ZBS glass although a small amount of Bi_2SiO_5 was crystallize, the sintering behavior could be interpreted as the one-stage sintering. The complete solid solution of Bi(Nb, Ta)O_4 with an orthorhombic structure was formed and the second phase of Bi_2SiO_5 was observed for all compositions. As the amount of Ta increased, the $Q\times f$ value increased in the low temperature region although the linear shrinkage decreased, indicating that the $Q\times f$ was improved by the addition of Ta. The dielectric constant was affected by the densification, i.e., the porosity. $Bi(Nb_{0.7}Ta_{0.3})O_4$ with 7 wt% ZBS glass sintered at 900°C demonstrated 35.8 in the dielectric constant (ε_r), 2,200 GHz in the $Q\times f$ value, and −48 ppm/°C in the temperature coefficient of resonant frequency (τ_f).

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References

1. H. Kagata, T. Inoue, J. Kato, I. Kameyama, T. Ishizaki, Ceram. Trans. **32**, 81 (1993)
2. T. Negas, G. Yeager, S. Bell, N. Coats, I. Minis, J. Am. Ceram. Soc., Bull. **72**, 80 (1993)
3. G. Wolfram, H.E. Gobel, Mater. Res. Bull. **16**, 1455 (1981)
4. S. Nomura, K. Toyama, K. Kaneta, Jap. J. Appl. Phys. **21**, L624 (1982)
5. S.I. Hirno, H. Takashi, A. Hattori, J. Am. Ceram. Soc. **74**, 1320 (1991)
6. V. Tolmer, G. Desqardin, J. Am. Ceram. Soc. **80**, 1997 (1981)
7. H. Kagata, T. Inoue, J. Kato, I. Kameyama, Jpn. J. Appl. Phys. **31**, 3152 (1992)
8. W. Choi, K.Y. Kim, M.R. Moon, K.S. Bae, J. Mater. Res. **13**, 2945 (1998)
9. O.A. Shlyakhtin, A.V. Orlov, Y.J. Oh, J. Electroceram. **17**, 405 (2006)
10. C.L. Huang, M.H. Weng, Mater. Lett. **43**, 32 (2000)
11. N. Wang, M.Y. Zhao, Z.W. Yin, Mater. Sci Eng. **B99**, 238 (2003)
12. B.W. Hakki, P.D. Coleman, IRE Trans. Microwave Theor. Tech. **MTT-8**, 402 (1960)
13. J.-M. Wu, H.-L. Huang, J. Non-Cryst. Solids **260**, 116–124 (1999)
14. K.P. Surendran, P. Mohanan, M.T. Sebastian, J. Solid State Chem. **177**, 4031–4046 (2004)
15. A.W. Sleight, G.A. Jones, Acta Cryst. **B31**, 2748–2749 (1975)
16. S. Georges, F. Goutenoire, P. Lacorre, J. Solid State Chem. **179**, 4020–4028 (2006)
17. F.G. Ewsuk, L.W. Harrison, F.J. Walezak, in *Ceramic powder science: part B*, ed. By G. L. Messing, E. R. Fuller, Jr., H. Hausner (Am. Ceram. Soc., Westerville, OH. 1988), p. 969
18. K.G. Ewsuk, in *Ceramic transactions*, vol. 15 ed. By K. M. Nair, R. Pohanka, and R. C. Buchaman (Am. Ceram. Soc., Westerville, OH, 1990), p. 279
19. S. Kemethmuller, M. Hagymasi, A. Stiegelschmitt, A. Roosen, J. Am. Ceram. Soc. **90**, 64 (2007)
20. C.-Y. Lee, R. Macquart, Q. Zhou, B.J. Kennedy, J. Solid State Chem. **174**, 310 (2003)
21. N. Wang, M.-Y. Zhao, Z.-W. Yin, Mater. Sci. Eng. **B99**, 238–242 (2003)
22. J.-M. Wu, H.-L. Huang, J. Non-Cryst. Solids **260**, 116 (1999)
23. H. Tumura, J. Am. Ceram. Soc. **73**, 93 (1994)