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Effect of V_2O_5 and CuO additives on sintering behavior and microwave dielectric properties of $BiNbO_4$ ceramics

CHENG-LIANG HUANG, MIN-HANG WENG, GAI-MING SHAN
Department of Electrical Engineering, National Cheng-Kung University, Tainan, Taiwan, ROC
E-mail: huangcl@mail.ncku.edu.tw

The influences of V_2O_5 and CuO additives on the sintering behavior and microwave dielectric properties of $BiNbO_4$ ceramics were investigated. The V_2O_5 and CuO additives lowered the sintering temperature of $BiNbO_4$ ceramics to the range 875 °C–935 °C. All $BiNbO_4$ compounds with additives had the orthorhombic structure. The dielectric constant ε_r was not significantly changed, while the unloaded *Q* value was affected with additives. The *Qf* value was found to be a function of the sintering temperatures and the amount of additives. It varied from 4500 to 15800 (GHz) and 1000 to 8000 (GHz) with additives V_2O_5 and CuO, respectively. The τ_f values were increased in positive values with V_2O_5 doped, while decreased in negative values with CuO addition. V_2O_5 and CuO additives effectively improved the densification and dielectric properties of $BiNbO_4$ ceramics. The correlation between the microstructure and the *Qf* value was observed with different additives.

1. Introduction

The rapid popularization of mobile communications has stirred up downsizing the transceiver for convenience of use. The effort has been concentrated upon the fabrication of a small resonator within the multilayed integrated circuit (MLIC) [1, 2]. To apply the multilayer technology, development of a dielectric material suitable for cofiring with internal conductors below the melting temperature of the metals have become a major focus. The search for high-dielectric constant materials with high temperature stability and a low dissipation factor was initiated. The development began with the search for a suitable low-firing-temperature dielectric, and then the modification of the electrical characteristics to meet the above requirements for the resonator. 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 [3, 4].

It is well known that bismuth-based dielectric ceramics are low-firing temperature materials and have been studied for piezoelectric materials or multilayer ceramic capacitors [5, 6]. Kagata *et al*. were the first to report the microwave dielectric properties of $BiNbO_4$ ceramics [7]. Small amounts of V_2O_5 and CuO were added in $BiNbO_4$ to densify the ceramics. The amounts of additives were selected so as to obtain a higher *Q* value. However, the effect of the amount of additives on the sintering temperatures and microwave dielectric properties of $BiNbO_4$ ceramics were not reported. It is interesting to clarify the relationship above. In this paper, $BiNbO_4$ ceramics were chosen as the host material to be sintered with two sintering aids, V_2O_5 and CuO. The sintering behavior and microwave dielectric properties of $BiNbO_4$ ceramics with different amount of additives were investigated. The resultant microwave properties were analyzed based on the densification, the microstructure and the amount of additives.

2. Experimental procedures

Specimen powders were prepared by a conventional solid-state reaction technique. The starting materials were high purity (>99.9%) Bi_2O_3 and Nb_2O_5. These powders were weighed according to the $BiNbO_4$ compositions. Mixtures were milled with ZrO_2 balls for 24 h in DI water and then dried. The dried powders were calcined at 800°C for 3 h. The calcined powders were remilled with different amount of V_2O_5 and CuO as the sintering aids and then sieved using a 100 mesh screen. The sieved powders were added with an organic binder and pressed uniaxially into disks at 100 Kg/cm^2. The disks were 11 mm in diameter and 5 mm in thickness. The pellets were sintered at temperatures from 855°C to 955°C for 3–6 h. The ceramic samples prepared with the sintering aids V_2O_5 and CuO showed a change in color from white to light yellow and black, respectively.

The crystalline phases were analyzed by means of an X-ray powder diffraction method using Cu-K_α radiation from 20° to 60° in 2θ. The microstructural analysis was observed by a scanning electron microscope. The densities of the sintered ceramics were measured using the Archimedes method. Measurements of the dielectric constant and the unloaded *Q* values on TE_{011}

mode at 6–8 GHz were completed by the post resonant method developed by Hakki and Coleman [8]. The temperature coefficient of the resonant frequency were obtained by measuring $TE_{01\delta}$ resonant frequency at 25°C (f_{25}) and 80°C (f_{80}) and applying to Equation 1.

$$\tau_f = \frac{f_{80} - f_{25}}{55 \times f_{25}} \times 10^6 \text{ (ppm/°C)} \qquad (1)$$

3. Results and discussion

Typical X-ray diffraction patterns of 0.5wt%-V_2O_5 added $BiNbO_4$ ceramics are shown in Fig. 1. $BiNbO_4$ is known to have a crystal structure of the orthorhombic-$SbTaO_4$ type below 1020°C, and to then transforms to the triclinic phase as the temperature goes higher. As shown in Fig. 1a, the calcined powder at 800°C exhibited the orthorhombic $BiNbO_4$ phase as the main crystalline phase with the existence of some other minor phases. In Fig. 1b–d, the sintering samples showed only a single orthorhombic $BiNbO_4$ phase over the sintering temperatures from 875°C to 955°C. Impurity phases were not detectable by XRD in any of the additive amounts. $BiNbO_4$ ceramics with the additions of CuO or CuO-V_2O_5 mixtures showed the same X-ray patterns. It suggested that the additive densified the $BiNbO_4$ ceramics and did not lower the phase transition temperature of the $BiNbO_4$ ceramics.

3.1. The $BiNbO_4$ system with V_2O_5 added

Properties of the $BiNbO_4$ ceramics with V_2O_5 added were functions of the sintering temperature and the amount of additives. The results are illustrated in Table I. It worth noting that the sinterability of the $BiNbO_4$ ceramics with less than 0.125 wt% V_2O_5 added was not improved well, even when the sintering temperature was at 955°C. The microwave dielectric properties of the $BiNbO_4$ with 0.125 wt% V_2O_5 added was found not practical for the application. It was some difference to the result that the $BiNbO_4$ ceramics could be dense with ultra small amount of additives (<0.07 wt%) at a lower temperature (875°C) [7]. In general, the bulk densities of the ceramics were dependent on the sintering temperature. High density ceramics can be obtained with high sintering temperatures for a given amount of

TABLE I Dielectric properties of the V_2O_5 added $BiNbO_4$ ceramics as functions of sintering temperature and amount of additive

The amount of V_2O_5 (wt%)	ST (°C)	Density (g/cm^3)	ε_r	Qf (GHz)	τ_f (ppm/°C)
undopant	1020	7.08	40	-	-
0.125	895	6.92	41	4500	-
	915	6.98	42	5600	6
	955	7.12	43	7000	
0.25	895	7.08	43	6900	-
	915	7.15	43	9400	13
	935	7.18	43	7800	-
0.5	875	7.19	44	14600	-
	895	7.21	44	15800	18
	915	7.20	44	15200	-
1	875	7.18	43	6000	-
	895	7.20	43	7600	23
	915	7.19	43	7000	-
2	875	7.20	43	4600	-

ST: sintering temperature.

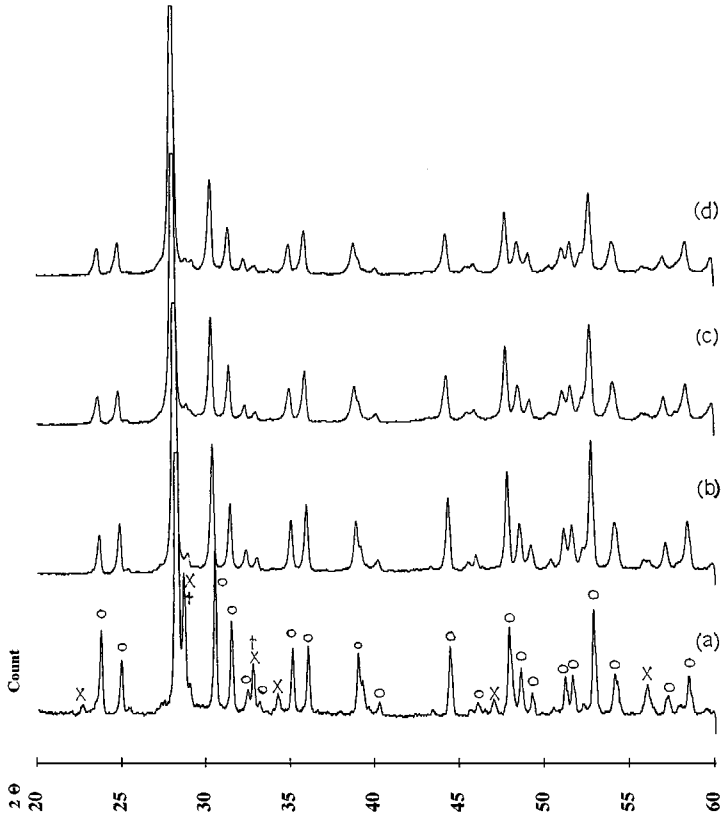

Figure 1 Typical XRD patterns of the 0.5 wt%-V_2O_5 added $BiNbO_4$ ceramics as a function of firing temperature. (a) calcined at 800°C (b) sintered at 875°C (c) 915°C and (d) 955°C (o: $BiNbO_4$, ×: $Bi_8Nb_{18}O_{57}$, +: $Bi_5Nb_3O_{15}$).

additive. However, too high a sintering temperature or too long a soaking time led to the densities of the ceramics decreasing owing to abnormal grain growth or cracks, then decreasing the electric properties of the ceramics as shown in Table I. The sintering temperature needed for maximum densities of ceramics gradually decreased from 935°C to 875°C as the amounts of V_2O_5 increased from 0.125% to 1%. The ε_r values as function of sintering temperature had the same trend as the bulk density of ceramic. The ε_r values saturated at about 42–44 in the dense $BiNbO_4$ ceramics.

The SEM micrographs of the pure and 0.5wt%-V_2O_5 added $BiNbO_4$ ceramics are shown in Fig. 2. The grains of pure $BiNbO_4$ ceramic grew slowly below 955°C and had a lot of pores, even when sintered at 1020°C as shown in Fig. 2a. In Fig. 2b–c, the pores of $BiNbO_4$ ceramic with V_2O_5 added were eliminated at a lower temperature. The grains sintered at 895°C were larger and more uniform than those sintered at 875°C.

The Qf values were strongly dependent on the amount of V_2O_5 added. The Qf values showed an increase from 4500 to 15800 GHz as the amount of V_2O_5 added increased from 0.125 wt% to 0.5 wt% followed by a decrease to 7000 GHZ as the V_2O_5 excess 0.5 wt%. The dielectric loss in the microwave region has an intrinsic and an extrinsic origin [8]. The intrinsic loss is caused by anharmonic phonon decay processes in the pure crystal lattice while the extrinsic losses were caused by crystal defects and grain boundaries. Since the $BiNbO_4$ ceramic showed a single phase over all sintering temperatures, it implied that the extrinsic loss dominated the dielectric loss of the $BiNbO_4$ ceramics. As shown in Fig. 2b–c, the grain was uniform and the grain boundary was reduced. The lattice imperfect was then also reduced. On increasing the amount of V_2O_5 from 0.5 wt% to 1.0 wt%, the sintering temperature of $BiNbO_4$ ceramics was lowered. Unfortunately, it also degraded the microwave dielectric properties. The reason was that too many additives caused a grain boundary phase or second phase in the grain and inhibited the grain growth, i.e., degraded the electric properties of ceramics.

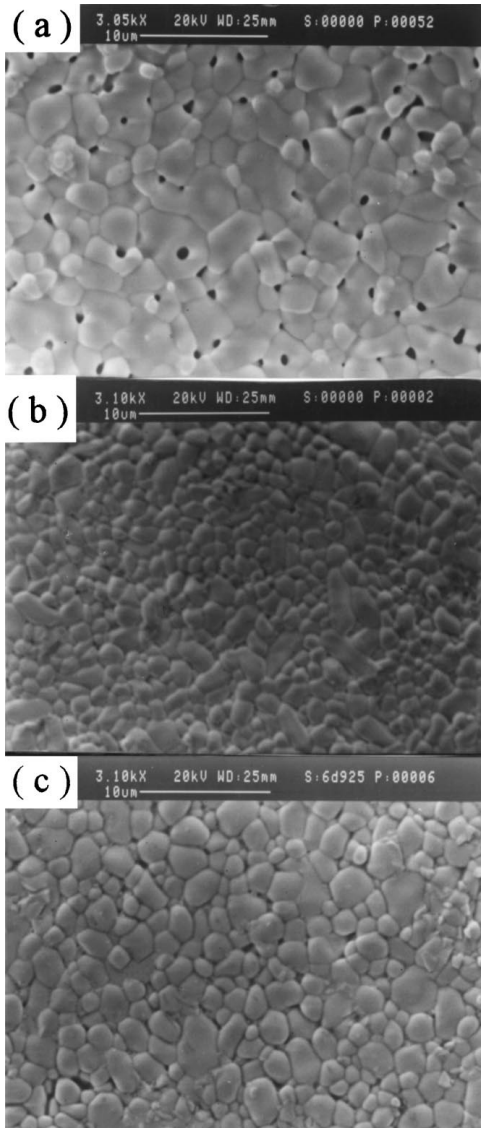

Figure 2 SEM micrographs of (a) the pure $BiNbO_4$ ceramics sintered at 1050°C (3 h), and 0.5 wt%-V_2O_5 added $BiNbO_4$ ceramics sintered at (b) 895°C (c) 915°C.

The τ_f values of the $BiNBO_4$ ceramics measured at the temperature with the maximum density increased from 13 ppm/°C to 23 ppm/°C as the amount of V_2O_5 increased from 0.25 wt% to 1.0 wt%. The τ_f value is related to the temperature coefficient of dielectric constant τ_ε and the expansion constant, α_L.

$$\tau_f = -\left(\frac{1}{2}\right)\tau_\varepsilon - \alpha_L \tag{2}$$

Since the magnitude of α_L is in general insignificant compared to that of τ_ε in the case of ceramics, it is clear that τ_f is directly influenced by τ_ε. The τ_ε value of dielectrics has been of interest for some time because it determines the stability of capacitors. It suggests that the τ_ε of $BiNbO_4$ ceramics with V_2O_5 added decreased in negative values.

The $BiNbO_4$ ceramics with 0.5 wt% V_2O_5 added sintered at 895°C showed better microwave dielectric properties $\varepsilon_r \sim 43$, $Qf \sim 15800$ (at 6.3 GHz), and $\tau_f \sim +18$ ppm/°C. It seemed that the higher ε_r value was due to higher relative density and the higher Qf value was caused by the larger grain size and more uniform grain as shown in Fig. 2c.

3.2. The $BiNbO_4$ system with CuO added

CuO is a well known sintering aid due to its low melting point. The microwave dielectric properties of $BiNbO_4$ ceramics with CuO as a function of sintering temperature and the amount of additives are shown in Table II. The SEM micrographs of the 0.5 wt% added $BiNbO_4$ ceramics sintered at 915°C and 935°C are shown in Fig. 3a and b, respectively. The grain size is around 50 μm. Lots of cracks were created in the grain due to CuO evaporation It was not normal grain growth, but formed the secondary recrystallization due to high sintering temperature or long soaking time [10]. Secondary recrystallization is likely to occur when continuous grain growth is inhibited by the present of impurities or pores. Secondary recrystallization affects both the sintering of ceramics and the resultant properties.

TABLE II Dielectric properties of the CuO added $BiNbO_4$ ceramics as functions of sintering temperature and amount of additive

The amount of CuO (wt%)	ST (°C)	Density (g/cm^3)	ε_r	Qf (GHz)	τ_f (ppm/°C)
0.25	895	7.01	42	6000	-
	915	7.10	43	7200	−13
	935	7.12	43	7000	-
0.5	895	7.03	43	6000	-
	915	7.12	43	8000	−18
	935	7.11	42	6300	-
1.0	895	7.08	42	5600	-
	915	7.13	42	5700	−28
	935	7.13	42	5200	-

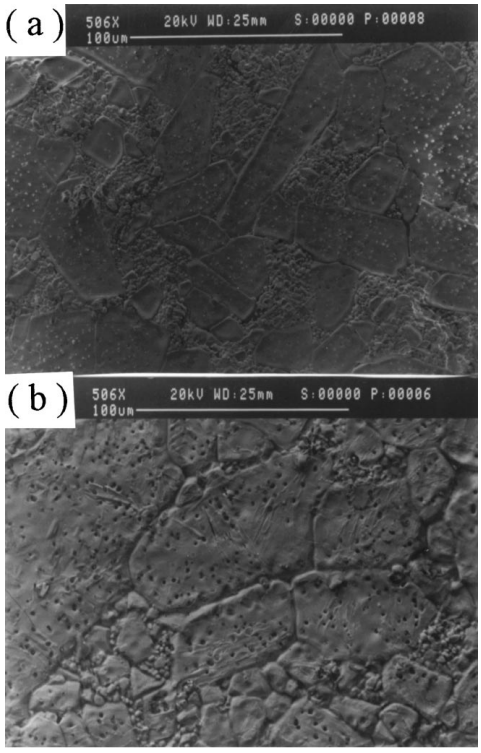

Figure 3 SEM micrographs of the 0.5 wt%-CuO added $BiNbO_4$ ceramics sintered at (a) 915°C (b) 935°C.

Occasionally grain growth has been discussed in the literature as if it were an integral part of the densification process. That this is not true can be seen by comparing the densities of $BiNbO_4$ ceramics with the V_2O_5 and CuO added. Even though the grain size of $BiNbO_4$ ceramics with CuO added was much larger than that with V_2O_5 added, the densities of $BiNbO_4$ ceramics with CuO added was smaller than that with V_2O_5 added at a certain firing temperature owing to the existence of the cracks in the grains.

An amount of CuO less than 0.125 wt% was found not to be enough to densify the ceramics effectively, and was sufficient when it was more than 2 wt%. As shown in Table II, the ε_r values also saturated at about 42–44 in the dense $BiNbO_4$ ceramics. The Qf values varied from 5000 to 9000. Comparing Table II to Table I, it was observed that the Qf values of the $BiNbO_4$ ceramics with CuO added were lower than those with V_2O_5 added. For some electric properties, either a large or a small grain size may contribute to improved properties. Excess grain growth is frequently harmful to electric properties. The secondary recrystallization degraded the dielectric properties of the $BiNBO_4$ ceramics. The resistance coefficient of the $BiNBO_4$ ceramics decreased owing to the addition of CuO. The unloaded Q value can be determined by Equation 3.

$$Q_u^{-1} = Q_d^{-1} + Q_c^{-1} + Q_r^{-1} \quad (3)$$

where Q_d^{-1}, Q_c^{-1} and Q_r^{-1} are the dielectric loss, conductor loss and radiation loss, respectively. The lower resistance of the ceramics resulted in a higher conductor loss and thus lowered the unloaded Q factor.

The τ_f values of the $BiNbO_4$ ceramics increased from −13 ppm/°C to −28 ppm/°C, as the amount of CuO increased from 0.25 wt% to 1.0 wt%. When increasing the amount of CuO, one could observe that the microwave characteristic decayed rapidly. The $BiNbO_4$ ceramics sintered at 915 °C with 0.5 wt% CuO added illustrated better microwave dielectric properties: $\varepsilon_r \sim 43$, $Qf \sim 8000$ (at 6.3 GHz), and $\tau_f \sim -18$ ppm/°C.

3.3. $BiNbO_4$ system with V_2O_5 and CuO mixtures added

In practical applications, it is desireable to adjust the τ_f value to be as near to 0 ppm/°C as possible. For this purpose, two or more compounds having positive and negative τ_f values were employed to form a solid solution or mixed phase. Since the τ_f values of the $BiNbO_4$ ceramics added with V_2O_5 and CuO were in the opposite direction, these two compounds were mixed to compensate the τ_f value. The microwave dielectric properties of V_2O_5/CuO added $BiNbO_4$ ceramics were also investigated. The results are demonstrated in Table III. The SEM micrographs of $BiNbO_4$ with V_2O_5 and CuO mixtures added are shown in Fig. 4. The grain was uniform and the grain boundary was reduced, then the lattice imperfect was also reduced. The τ_f values were actually improved with the addition of mixtures. It revealed that with 0.1 wt% CuO-0.4 wt% V_2O_5 mixture added, the τ_f value effectively decreased to 7.8 ppm/°C while Qf value still remained as high as 20400 (GHz).

TABLE III Dielectric properties of the CuO and V_2O_5 mixtures added $BiNbO_4$ ceramics as functions of sintering temperatures and amount of additives

The amount of V_2O_5 (wt%)	The amount of CuO (wt%)	ST (°C)	Density (g/cm^3)	ε_r	Qf (GHz)	τ_f (ppm/°C)
0.4	0.1	875	7.12	43	18500	-
		895	7.15	43	20400	7.8
		915	7.18	43	19000	-
0.25	0.25	875	7.08	43	16000	-
		895	7.10	43	20000	−8.2
		915	7.12	43	18600	-
0.1	0.4	875	7.07	43	6800	-
		895	7.12	43	7200	−14
		915	7.12	42	6300	-

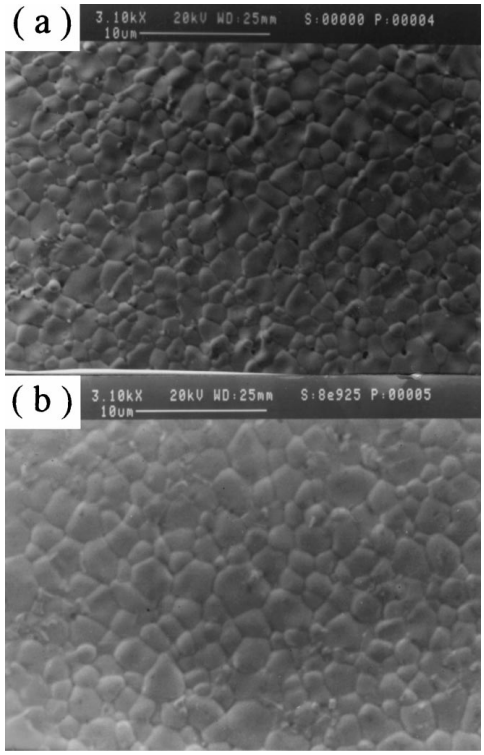

Figure 4 SEM micrographs of the 0.1 wt% CuO-0.4 wt% V_2O_5 mixture added $BiNbO_4$ ceramics sintered at (a) 875°C (b) 895°C.

4. Conclusions

A low-temperature microwave dielectric material $BiNbO_4$ was developed. The influence of the amount of CuO and V_2O_5 additives on the sintering and microwave dielectric properties of $BiNbO_4$ ceramic was investigated. The $BiNbO_4$ ceramics with V_2O_5 added had better sintering and microwave dielectric properties than those with CuO added. The proper amount of sintering aids, either CuO or V_2O_5, for $BiNbO_4$ ceramics was in the ranges of 0.25 wt%∼1 wt%. The delectric constant ε_r was not significantly changed, while the unloaded Q values were affected with additives. The τ_f values were increased in positive values with V_2O_5 dopant while they decreased in negative values with CuO doping. When doped with 0.1 wt% CuO and 0.4 wt% V_2O_5, the $BiNbO_4$ ceramics showed excellent microwave dielectric properties: $\varepsilon_r \sim 43$, $Qf \sim 20400$ (at 6.3 GHz), and $\tau_f \sim +7.8$ ppm/°C.

Compared to other low-firing temperature microwave dielectric materials, $BiNbO_4$ ceramics have not only better microwave dielectric properties but also adjustable τ_f values associated with the variations in amount of additives. The sintering temperature is considered low for a glass-free dielectric material.

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References

1. S. T. ISHIZAKI, M. FUJITA, H. KATAGA, T. UWANO and H. MIYAKE, *IEEE Trans. Microwave Theory & Tech.* **MTT-42** (1994) 2017.
2. R. PREGLE, *ibid.* **MTT-18** (1970) 278.
3. T. TAKADA, S. F. WANG, S. YOSHIKAWA, S. T. JANG and R. E. NEWNHAM, *J. Am. Ceram. Soc.* **77** (1994) 1909.
4. *Idem., ibid.* **77** (1994) 2485.
5. S. I. HIRNO, TAKASHI, HAYASHI and A. HATTORI, *ibid.* **74** (1991) 1320.
6. H. C. LING, M. F. YAN and W. W. RHODESM, *ibid.* **73** (1990) 1106.
7. H. KAGATA, T. INOUE, J. KATO and I. KAMEYAMA, *Jpn. J. Appl. Phys.* **31** (1992) 3152.
8. B. W. HAKKI and P. D. COLEMAN, *IEEE Trans. Microwave Theory & Tech.* **MTT-8** (1960) 402.
9. R. ZURMUHLEN, E. COLLA, D. C. DUBE, J. PETZELT, I. REANEY, A. BELL and N. SETTER, *J. Appl. Phys.* **76** (1994) 5864.
10. W. D. KINGERY, H. K. BOWEN and D. R. UHLMANN, "Introduction to Ceramics," 2nd ed. (J. Wiley, New York, 1976) p. 461.

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