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Control of coring effect in $BaTi_4O_9$ microwave dielectric ceramics by doping with Mn^{4+}

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Abstract

In the present work, we have attempted to reduce the effect of coring effect in the titanate ceramic system $BaTi_4O_9$ (BT4) by doping it with Mn^{4+}. The microwave dielectric $BaTi_4O_9$ ceramics doped with 0, 0.5 and 1.0 mol% Mn^{4+} were synthesized by conventional ceramic processing route. The XRD studies confirmed a single phase crystalline structure for all the ceramic samples studied. The SEM micrographs of the ceramics reveal a microstructural change leading towards a more uniform grain size distribution as the Mn^{4+} content increases to 1.0 mol%. In the low frequency region (100 Hz to 1 MHz), the temperature stability of dielectric properties exhibits a marked improvement with the increasing amount of Mn^{4+} in the ceramic system. In the microwave frequency region (9.3 GHz), Q-factor increases from 11,625 GHz to 46,500 GHz for $BaTi_4O_9$ ceramic doped with 1.0 mol% Mn^{4+}. The present paper reveals that the commonly observed degradation of dielectric properties due to coring effect in the $BaTi_4O_9$ ceramic system can be controlled by doping it with an appropriate quantity of Mn^{4+}.

Keywords: A. Calcination; A. Sintering; B. grain size; C. Dielectric properties

1. Introduction

The high speed communication system and miniature size components augment the rapid progress of the wireless communication industry. For achieving the higher speed and producing miniature size components, materials having high dielectric constant (ε') and high quality factor with high temperature stability are required [1–3]. The improved performance of the dielectric resonators (DR) leads to the rapid progress in the commercial wireless technologies such as mobile phones, direct broadcasting satellite (DBS) and global positioning systems [1–5]. The size of the dielectric resonator is proportional to $1/\sqrt{\varepsilon'}$, and so in order to reduce size of the component higher ε' materials are required [4]. For obtaining a temperature stable microwave dielectric component, the resonant frequency of the dielectric material is required to remain almost unchanged over a large range of temperature (-20 °C to $+80$ °C), thereby resulting in a negligibly small temperature co-efficient of resonant frequency (τ_f) [1,2]. To maintain the insertion loss of the microwave device component at a very low level, the quality factor $Q(=1/\tan\delta)$ of the dielectric material needs to be very high (Q»3000 at 1 GHz) [1–3]. These stringent requirements of very high quality factor Q and very low τ_f have restricted many of the dielectrics to be qualified as microwave dielectrics [2,3,5]. The ferroelectric ceramics generally possess very high dielectric constant but their dielectric properties are not stable with temperature and τ_f is very high while Q is very low; so they are not suitable candidates for microwave dielectric ceramics [5]. Only few of the ferroelectrics like $SrTiO_3$ which are in paraelectric phase at room temperature due to their low Curie temperature (T_c) satisfy the conditions required for microwave dielectric ceramics [3,5].

Many of the commercially available high ε' microwave dielectrics are titanate based ceramics such as $Zr_{1-x}Sn_xTiO_4$, $BaTi_4O_9$, $Ba_2Ti_9O_{20}$, $MgTiO_3$, $CaTiO_3$ etc. [3–5]. As these titanates require very high temperature (above 1300 °C) for

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sintering, very often dielectric properties are degraded because of the compositional and structural fluctuation due to the reduction of Ti^{4+} to Ti^{3+} (coring effect) [3,5–7]. It is thus of utmost importance for their practical applicability to control the unwanted coring effect and optimize the Q-factor (or reduce the dielectric loss) of these titanate based microwave ceramics.

$BaTi_4O_9$ is a popular dielectric ceramic material for microwave communication [6,8,9]. Many workers have worked on this system to find a solution to the compositional fluctuation by using various types of dopants or subtituents such as Ca, Sr, Zr, Pb, Sn, Co, Y, Sm, Nd, W etc. [9–12]. Yang et al. have tried to control the degradation of the dielectric properties of the BT4 system by sintering it at lower temperature ~1200 °C with the addition of low melting glasses [13,14]. Other workers also sintered this system at reduced temperature by starting with nanoscale powders prepared by chemical route [5,15] and by using a reaction sintering technique [16]. Sebastian [3] and Reaney et al. [5] proposed Mn^{2+} as an effective dopant for controlling the problem of coring effect and improving the Q-factor of the titanate ceramics. But no report exists in literature on doping of $BaTi_4O_9$ system with Mn^{4+}. This paper discusses the effectiveness of Mn^{4+} doping in enhancing the dielectric properties and hence in turn controlling the coring effect in $BaTi_4O_9$ ceramic system.

2. Experimental

Microwave dielectric $BaTi_4O_9$ ceramic system was synthesized by using the conventional solid sate sintering route. The starting ingredients were AR grade powders of $BaCO_3$ and TiO_2, MnO_2 and $CaCO_3$. The powders were homogeneously mixed by ball milling in distilled water medium and then dried in an oven. The dried powder was then calcined at 1075 °C for 4 h. The calcined powder was then ball milled again in water medium for 12 h at the speed 100 rpm while maintaining a mass ratio of 1:5 for powder and balls. The ball milled powder was then dried and sieved. The processed powder was then pressed in the form of pellets by using a hydraulic press and the pellets were sintered at 1375 °C for 4 h. The experimental density of the sintered specimens was measured using Archimedes principle. The crystalline phases of the samples were characterized by X-ray diffractometer (Discover S8). The microstructures of the fractured surfaces were studied using SEM (Leo 1430, Japan). Temperature dependence of dielectric constant and loss tangent at lower frequency (1 kHz) was measured with an impedance analyzer (Wayne Kerr 6505B). The values of dielectric properties (ε' and Q) at microwave frequencies (9.3 GHz) were measured by using a cavity perturbation technique with the help of a vector network analyzer (HP 8510C).

3. Result and discussion

3.1. Structural analysis

Fig. 1(a) shows the XRD patterns of the undoped, 0.5 mol% and 1 mol% Mn^{4+} doped $BaTi_4O_9$ ceramic samples. The presence of single phase orthorhombic structure for the doped and undoped BT4 ceramic samples is evident from this figure (matched with JCPDS Card no. 340070). This result indicates that Mn^{4+} dopants have completely diffused into the $BaTi_4O_9$ lattice to form a homogeneous solid solution. It can be noted from Fig. 1(a) that the positions of the diffraction peaks of the ceramics shift slightly to higher angles indicating a small shrinkage of lattice cell volume as Mn^{4+} content increases in the ceramics. Partial substitution of Mn^{4+} (ionic radius = 0.60 Å) for Ti^{4+} (ionic radius = 0.64 Å) gives rise to the small shrinkage of cell volume. Fig. 1(b) shows the variation of room temperature lattice parameters (a,b,c) and unit cell volume (V) calculated from the X-ray diffraction data, with Mn^{4+} content in ceramics. It can be seen that the values of lattice parameters "a" and "b" decrease while that of lattice parameter "c" increase, resulting in an overall contraction in cell volume, with the increase of Mn^{4+} doping level in the ceramic system. The contraction in lattice cell volume also indicates the solubility of Mn^{4+} ions in the $BaTi_4O_9$ system by replacing larger Ti^{4+} ions [9].

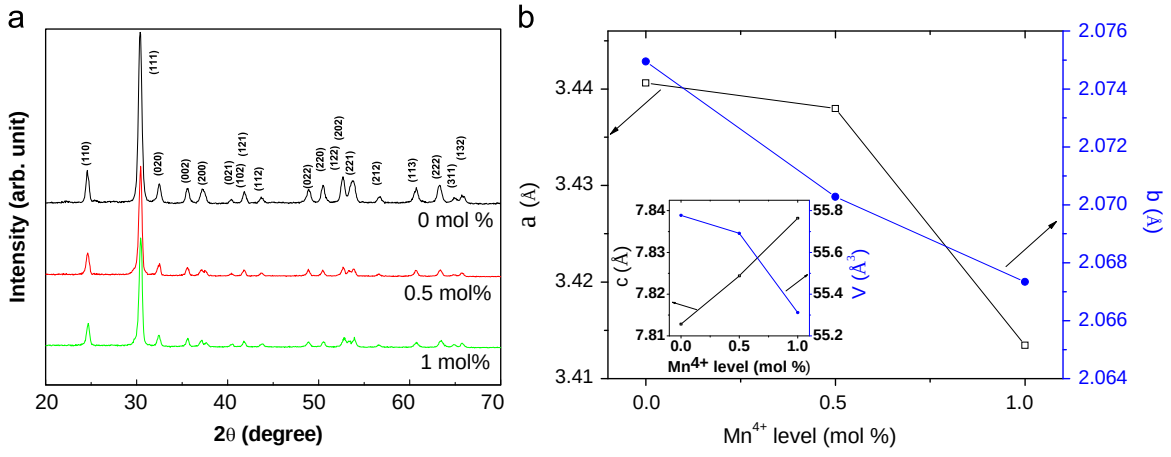

Fig. 1. (a) XRD patterns, and (b) Lattice parameters, of 0, 0.5 and 1.0 mol% Mn^{4+} doped $BaTi_4O_9$ ceramics.

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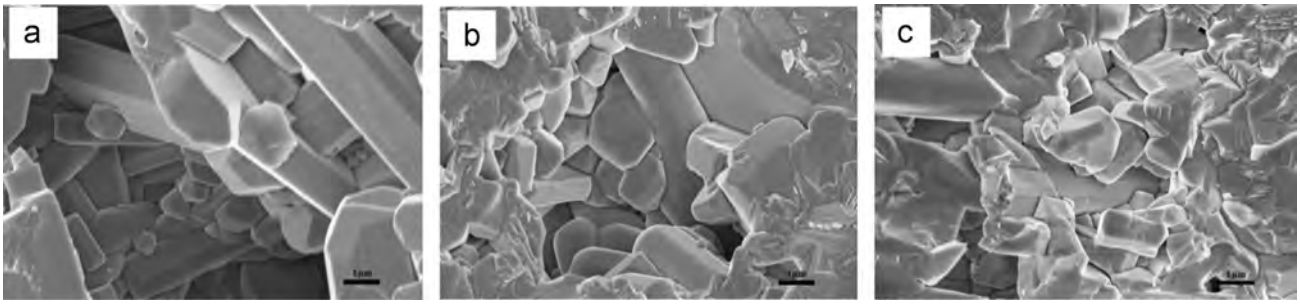

Fig. 2. SEM Micrographs of (a) 0 mol% (b) 0.5 mol% and (c) 1.0 mol% Mn^{4+} doped $BaTi_4O_9$ ceramics.

3.2. Microstructural characteristics

Fig. 2 shows the SEM micrographs of 0, 0.5 and 1.0 mol% Mn^{4+} doped $BaTi_4O_9$ ceramic samples. It can be noted that there are two types of grains present in all the samples-smaller grains and elongated rice shaped grains. Appearance of such elongated grains in $BaTi_4O_9$ system has also been observed by other workers [8,17,18]. For the undoped $BaTi_4O_9$ system, the average grain size varies from 0.6 μm to 0.75 μm for the smaller grains and from 1.55 μm to 1.80 μm for the elongated grains. In the case of 0.5% Mn^{4+} doped $BaTi_4O_9$ sample, the average size of the smaller grains varies from 0.8 μm to 0.85 μm while the rice shaped grains possess an average size of about 1.75 μm. The relative population of elongated grains is reduced when the Mn^{4+} doping level is increased in the ceramics. In 1% Mn^{4+} doped $BaTi_4O_9$ system, the average size of the smaller grains further increases while that of the elongated grains decreases, thereby giving rise to a more uniform grain size distribution with an overall average grain size of about 1 μm.

3.3. Dielectric properties

Fig. 3 shows the variation in permittivity as a function of temperature for the $BaTi_4O_9$ ceramics in the lower frequency region (1 kHz). It can be noted that, for all the samples, there is negligible change in the value of dielectric constant with the change of temperature. The temperature coefficients of dielectric constant (τ_ε) of all the samples determined using the relation $\tau_\varepsilon = (\delta\varepsilon'/\delta t) \times 1/\varepsilon'$ are tabulated in Table 1. The value of τ_ε for all the samples remains significantly low and decreases further indicating an improvement in the quality of the ceramic system with the increase of Mn^{4+} content. The temperature coefficient of resonant frequency (τ_f) is a function of the temperature coefficient of dielectric constant (τ_ε) and is related by the expression [3–5]:

$$\tau_f = -1/2\tau_\varepsilon - \alpha$$

where α is the coefficient of thermal expansion. The low value of τ_ε thus predicts a low value of τ_f for the samples studied. Due to experimental limitations the value of τ_f could not be measured directly.

The values of the dielectric constant (ε') and quality factor (Q) measured at 9.3 GHz (microwave frequency region) are shown in Table 1. The values of room temperature dielectric constant of the doped and undoped $BaTi_4O_9$ ceramics remain almost unchanged in the low frequency region (Fig. 3) and

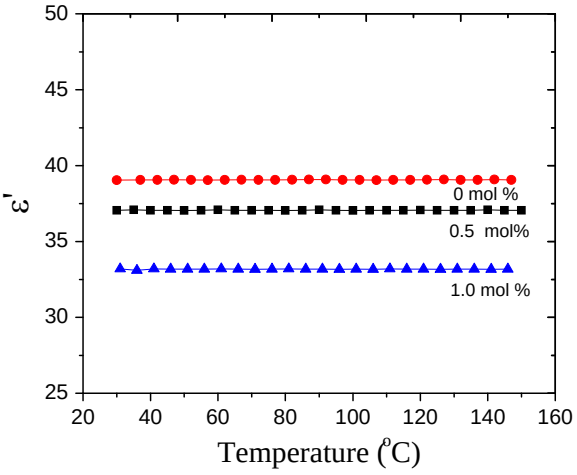

Fig. 3. Temperature variation of dielectric constant of 0, 0.5 and 1.0 mol% Mn^{4+} doped $BaTi_4O_9$ ceramics.

microwave frequency region (Table 1). This indicates a very small dispersion in the value of dielectric constant with frequency which is an evidence for high quality of the prepared ceramic samples.

In the $BaTi_4O_9$ based ceramics studied, it is observed that the value of dielectric constant (ε') slightly decreases and tangent loss ($\tan\delta$) significantly decreases (or Q-factor significantly increases) with the increase of doping level of Mn^{4+}. The dielectric loss of a microwave ceramic material is due to both intrinsic and extrinsic factors [1–3]. The origin of the intrinsic losses is due to the interaction of the applied ac field with the phonons of the material. The intrinsic dielectric losses depend on the crystal symmetry and are observed in single crystals [1–6,18–20]. In ceramic samples, the dielectric losses are dominated by the extrinsic factors as the crystalline structures of ceramics are far away from possessing perfect single crystal symmetry. Extrinsic losses are due to the imperfection in the crystal structure such as dopant or impurity atoms, dislocations, grain boundaries, vacancies, microcracks, microstructural defects, order–disorder behavior, secondary phases etc. [1–6,18–20]. Most of the extrinsic factors are process dependent and can be minimized. In the cases studied, during the sintering of these titanate ceramics at very high temperature (> 1300 °C for 4 h), there is partial reduction of Ti^{4+} to Ti^{3+} [1–3,5,6]. This is often observed as darkish cores in the titanate samples (coring effect), which causes degradation in the Q-factor [3,5]. This effect is more prominent during

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Table 1
Several properties of Mn^{4+} doped $BaTi_4O_9$ ceramics.

Amount of MnO_2 (mol%)	Densification (%)	ε' (at 9.3 GHz)	tan δ (at 9.3 GHz)	Q	$Q \times f$ (GHz)	τ_ε (ppm/°C)
0	98	40	0.0008	1250	11,625	+30
0.5	97	37	0.0004	2500	23,250	+20
1.0	95	33	0.0002	5000	46,500	+5

the sintering of larger components as the outer regions of the ceramic sinter and the sintered layer acts as a seal which prevents transport of oxygen to the core. Due to the lack of oxygen at the core there is creation of oxygen vacancies or titanium interstitials [1,5]. The presence of vacancies in the lattice tends to increase the anharmonicity of the lattice vibrations and dampening of the phonon modes and hence a degradation in the Q-factor [1–3,5,14]. In the present investigation, oxidation state of Mn^{4+} present in MnO_2 may co-exist in Mn^{2+} and Mn^{3+} states and enter into the lattice structure of the these titanate ceramics to substitute Ti^{4+} ion [2]. When Mn^{4+} is doped in the system, it helps to maintain Ti^{4+} due to the following reaction: -*

$$Mn^{4+} + Ti^{3+} \rightleftharpoons Mn^{3+} + Ti^{4+}$$

$$Mn^{3+} + Ti^{3+} \rightleftharpoons Mn^{2+} + Ti^{4+}$$

and, thus controls the reduction of Ti^{4+} to Ti^{3+} [1–3,5,8]. Mn^{4+} acts as a compensator for defect equilibrium helping to maintain Ti^{4+} during cooling. The degradation of Q-factor in BT4 can thus be controlled by doping with a small amount of Mn^{4+}.

The observed phenomena can also be explained in terms of conduction mechanism. When Mn^{4+} is doped in $BaTi_4O_9$ ceramics, large numbers of ionized oxygen vacancies and conduction electrons are created during sintering according to the equation:

$$O_o \rightleftharpoons \frac{1}{2} O_2 + V_o + 2e$$

To maintain the equilibrium state of the electron concentration, the produced electrons are almost fully delocalized by hopping motion from one titanate site to another. Mn^{4+} ions are more reducible than the Ti^{4+} ions and so electrons are trapped at these sites [2,5]. The hopping motion of the trapped electrons from one Mn site to another is almost prohibited. The conduction electrons are localized on these Mn sites; this results in a drop of carrier concentration and leads to decrease of conductivity [5]. Due to the decrease in conductivity, dielectric loss is decreased and Q-factor is increased with Mn doping.

4. Conclusions

High value microwave dielectric ceramic system $BaTi_4O_9$ doped with Mn^{4+} has been prepared by using conventional solid state reaction route. The X-ray diffraction studies confirmed a single phase crystalline structure for the ceramic system studied. The microstructural study shows the presence of two types of grains: small-size grains and rice-shaped grains in all the samples studied. With the increase of Mn^{4+} doping level in BT4 system, the size of the smaller grains increase while the density of rice shaped grains reduces, thereby resulting in a more uniform grain size distribution in the system. The temperature variation of the dielectric constant of the samples indicates an improvement in their temperature stability as the Mn^{4+} doping level increases. The study of the dielectric properties in the microwave frequency region (9.3 GHz) shows that the quality factor increases from 11,625 GHz to 46,500 GHz for $BaTi_4O_9$ when 1 mol% Mn^{4+} is doped in the system. The present paper reveals that the degradation of the quality factor due to coring effect in $BaTi_4O_9$ ceramic can be controlled by doping it with a suitable amount of Mn^{4+}.

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