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Effects of $LnAlO_3$ (Ln = La, Nd, Sm) additives on the properties of $Ba_{4.2}Nd_{9.2}Ti_{18}O_{54}$ ceramics

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Abstract

The effects of $LnAlO_3$ (Ln = La, Nd, Sm) additives on the microstructure and the dielectric properties of $Ba_{4.2}Nd_{9.2}Ti_{18}O_5$ (BNT) materials have been investigated. The microstructure of BNT doped with $NdAlO_3$ was analyzed using X-ray diffraction and scanning electron microscopy (SEM). Over 10 wt.% additions of $NdAlO_3$ diminished grain growth and the densifications process. In addition, typical columnar grain morphology observed in BNT ceramics was transformed to quasi-rectangular shapes accompanied by increasing porosity. XRD analysis did not reveal any second phases or modification of the BNT crystal structure. The addition of small amounts of $LnAlO_3$ ($\leq$10 wt.%) increased the Q values remarkably and improved the TCf. The relative permittivity and the TCf values showed a linear decrease with increasing additions of $LnAlO_3$. It was observed that near zero TCf values can be achieved with addition of $LnAlO_3$ dopants to BNT ceramics. The Q values exhibited a non-linear behaviour with $LnAlO_3$ additions with maxima attained at approximately 10 wt.% $LnAlO_3$.

Keywords: Dielectric properties; $BaTiO_3$ and titanates; $LnAlO_3$

1. Introduction

The growing industrial demand in the early 1980s for miniaturization of microwave devices stimulated research into ceramic materials with high relative permittivity based on $BaO–Ln_2O_3–TiO_2$ (BLT) where Ln^{3+} is a lanthanide species. The earliest work on these systems is credited to Bolton[1] and Kolar et al.[2] Temperature stable dielectric ceramics with high relative permittivities (70–90) and low losses (Qf = 5000–9000 GHz) have been developed in these systems.[3–6] The crystal structure of BLT ceramics belongs to the tungsten–bronze structural family and consists of a three dimensional framework of corner sharing perovskite-like TiO_6 octahedra linked at the corners in a complex way to yield three types of openings: large pentagonal sites, diamond sites and small triangular sites. According to Ohsato[7] the rare earth cations occupy the rhombic channels (diamond sites), Ba^{2+} cations fill the pentagonal channels and the remaining Ba ions share the rhombic channels with the lanthanides. The triangular channels are empty. The dielectric ceramics with the best properties consist almost exclusively of one phase with formula $Ba_{6-3x}Ln_{8+2x}Ti_{18}O_{54}$, where the limits of the solid solubility are generally $0 < x < 0.8$ depending on the lanthanide cation.[3–6] The compound forms for the large and intermediate size rare earths, for example, Sm^{3+}, Pr^{3+}, La^{3+} and Nd^{3+}. The solid solution involves the mixing of some of the Ba^{2+} and Ln^{3+} with vacancies on the rhombic sites in the appropriate ratio to maintain charge neutrality. In these ternary systems, TCf and Qf values are very strong functions of the composition. For $Ba_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$ (Ln = Nd^{3+}), where $x = 0.6$, a high permittivity of 88, and high $Qf \approx 8300$ GHz, have been reported.[8] However, this system has a high TCf of about 76 ppm/°C, thus a lot of work has been done to tune TCf to near zero including partial substitution of Nd^{3+} with Sm^{3+} in the rhombic channels.[9] Additives such as Pb^{2+} and Bi^{3+} have also been found to be very helpful in stabilizing the low TCf behavior while increasing the permittivity but they do not have favourable effects on Q values.[10,11] Addition of $MnCO_3$ and ZnO on BNT has also been shown to decrease the TCf.[12,13] In the present study, $LnAlO_3$ (Ln = La, Nd, Sm) ceramics have been used as additives in an effort to tune the TCf of BNT ceramics to near zero while improving the Qf values. Unlike BNT ceramics, $LnAlO_3$ ceramics feature pseudo-cubic perovskite structure. Cho[14] reported that the $LnAlO_3$ (Ln = La, Nd, Sm) materials have high Qf values of over 55000 GHz and negative TCf of about −30 ppm/°C to −70 ppm/°C and moderate permittivities in the range of 20–24. The effects of $LnAlO_3$

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additions on the microwave dielectric properties of BNT have therefore been investigated. The structural developments due to the addition of $LnAlO_3$ to the main component have been monitored using X-ray diffraction analysis and scanning electron microscopy (SEM).

2. Experimental procedure

Samples were prepared by the conventional solid-state reaction. Reagent-grade $BaCO_3$, Nd_2O_3, TiO_2, La_2O_3, Sm_2O_3 and Al_2O_3 with the purity of over 99.5 wt.% were used as raw materials. The starting materials were mixed according to the stoichiometries of $Ba_{4.2}Nd_{9.2}Ti_{18}O_{54}$ and $LnAlO_3$ (Ln = La, Nd, Sm) using deionised water and zirconia milling media. The mixtures were calcined separately, such that, $Ba_{4.2}Nd_{9.2}Ti_{18}O_{54}$ and $LnAlO_3$ were calcined at 1250 °C and 1200 °C for 2 h, respectively. Different amounts of $LnAlO_3$ were added to the calcined BNT. The materials were then remilled for 3 h and dried. PVA binder was added and powders pressed into disks 15 mm in diameter and a thickness of 7–10 mm at 100 MPa. The samples were sintered at 1320–1380 °C for 2 h in an air atmosphere with a heating rate of 300 °C/h and a cooling rate of 100 °C/h. The bulk densities of the samples were measured by Archimedes' method. The microstructure of the as-sintered surface was studied using scanning electron microscopy model JEOL JSM 5610 LV. The X-ray diffraction experiments were performed on bulk samples using a RIGAKU D/max-RC diffractometer operating at 40 kV. A continuous scan was carried out using monochromatic Cu Kα radiation filtered through a Ni foil with 2θ angles in the range of 10–70° with a step size of 0.02° and a speed of 15°/min. The dielectric properties were measured using dielectric post resonator technique developed by Hakki and Coleman.[15] The temperature coefficient of the resonant frequency (τ_f) was also measured by the same method in the temperature range of 25–75 °C.

3. Results and discussions

Fig. 1 shows the variation of bulk densities as a function of the addition of $NdAlO_3$ sintered at temperatures between 1320 °C and 1380 °C for 2 h. The sample densities at about 5.6 g/cm^3 were not significantly affected by sintering temperature or addition of up to 10 wt.% of $NdAlO_3$. However, with increased additions of $NdAlO_3$, high sintering temperatures were required to achieve good densification mainly due to the high sintering temperature of $NdAlO_3$ (over 1500 °C).

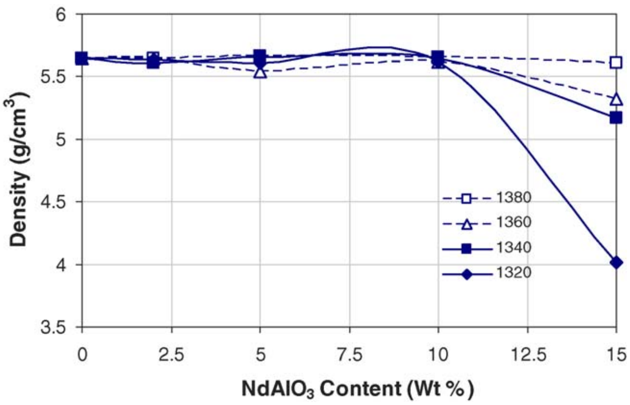

Fig. 1. The variation of bulk density with amounts of $NdAlO_3$ added into BNT sintered at different temperature for 2 h.

Typical SEM micrographs of $NdAlO_3$ doped $Ba_{4.2}Nd_{9.2}Ti_{18}O_{54}$ ceramics sintered at 1340 °C for 2 h are shown in Fig. 2. The ceramics show typical columnar grain morphology usually observed in $Ba_{6-3x}Ln_{8+2x}Ti_{18}O_{54}$ (Ln = Nd, Sm) ceramics.[16,17] With increasing content of $NdAlO_3$ additions the grain sizes tend to become smaller. In addition, the fine columnar grain structure observed is diminished and at 15 wt.% $NdAlO_3$ the grains feature quasi-rectangular shape. Significant amount of porosity is also observed at higher concentrations of $NdAlO_3$. No evidence of second phases were observed in the SEM micrographs. Therefore, small additions $NdAlO_3$ to BNT does not affect the densification while above 10 wt.%, $NdAlO_3$ additions suppressed the grain growth and hindered the densification process. Fig. 3 shows the XRD patterns of $Ba_{4.2}Nd_{9.2}Ti_{18}O_{54}$ ceramics with different amounts of $NdAlO_3$ added and sintered at 1340 °C for 2 h. All the XRD patterns can be assigned to that of the orthorhombic tungsten bronze type compounds, designated as $(BNT)_{114}$ and $(BNT)_{115}$.[8,12] With increasing addition of $NdAlO_3$ with perovskite phase on BNT, extra peaks were not observed even at the highest concentration of 15 wt.%. It is suggested any possible reflections from a secondary perovskite phase might overlap with the tungsten bronze structure reflections. No significant changes in the XRD patterns were observed as reported by Silva et al.[16] where similar perovskite-type $(Li_{1/2}Nd_{1/2})TiO_3$ were added to BNT structure.

Fig. 4 shows the dielectric constant of BNT ceramics with increasing additions of $LnAlO_3$ (Ln = La^{3+}, Nd^{3+} and Sm^{3+}) sintered at 1340 °C for 2 h. In all the compositions, additions of rare earth aluminates deteriorate the dielectric constant. The observed change in permittivities is attributed to the low permittivities of the dopants. However, the highest dielectric constants were observed with addition of $LaAlO_3$ up to 10 wt.% while $SmAlO_3$ had the lowest values. Fig. 5 shows the change in TC*f* values with additions of $LnAlO_3$. In a similar to the variation in permittivity, the TC*f* values show a linear decrease with increasing content of the additives. $LaAlO_3$ decreases the TC*f* of BNT from +80 ppm/°C to +8.6 ppm/°C for samples with 15 wt.% additions. However, a near zero TC*f* value of −0.7 ppm/°C was achieved with 10 wt.% $NdAlO_3$. For the $SmAlO_3$ derivative, a near zero TC*f* value is expected at approximately 8.5 wt.%. In all the compositions it is apparent that the TC*f* values of tungsten bronze structured BNT ceramics can be tuned to near zero with additions of perovskite structured rare earth aluminates. Fig. 6 shows a non-linear variation in *Qf* values of BNT with various additions of $LnAlO_3$ ceramics. The entire range of compositions investigated exhibit an initial increase in the *Q* values with a maxima attained at approximately 10 wt.% additions of $LnAlO_3$ followed by a sharp drop at 15 wt.%. The high

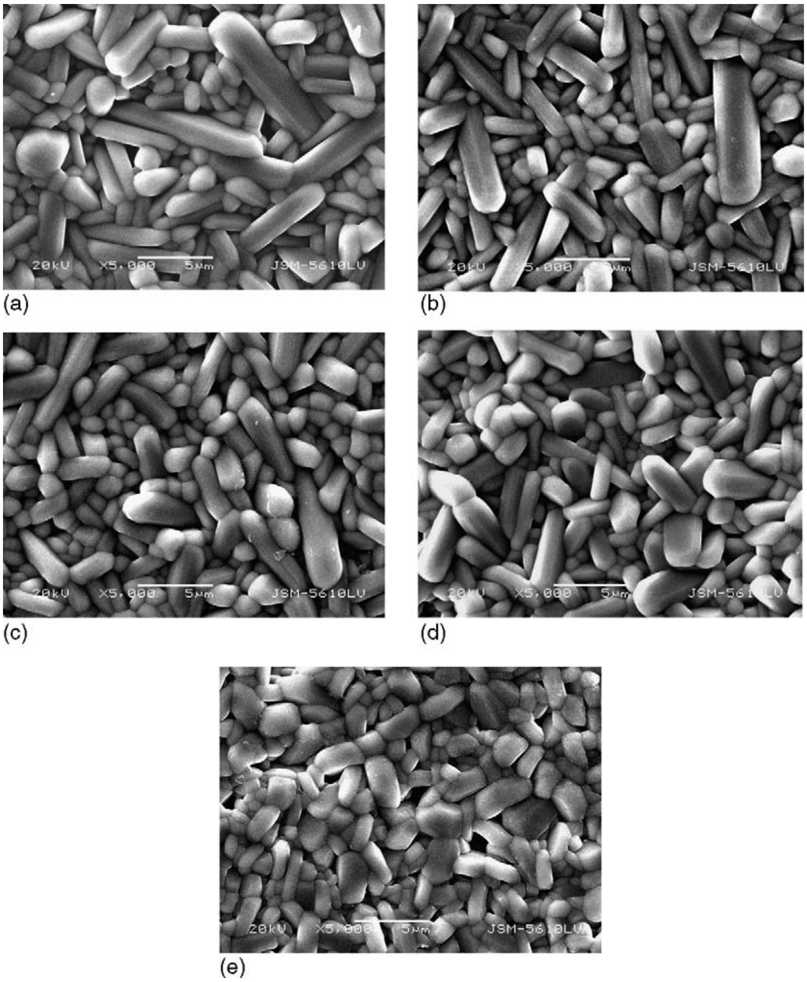

Fig. 2. Typical SEM micrographs of BNT sintered at 1340 °C for 2 h with $NdAlO_3$ added where (a) 0 wt.%; (b) 2.0 wt.%; (c) 5.0 wt.%; (d) 10.0 wt.%; and (e) 15.0 wt.%.

Q values of $LnAlO_3$ might attribute to the increase in the *Q* values of BNT under the condition of good densification, however it is hard to achieve good densification with the additions of 15 wt.% $LnAlO_3$ at the sintering temperature around 1340 °C, which was shown in Figs. 1 and 2(e), as a result, the *Q* values decrease. What's more, whether larger amounts of $LnAlO_3$ additions would enhance *Q* values of BNT at a higher temperature need further investigation. *Qf* values as high as 11400 GHz were achieved with addition of 10 wt.% $NdAlO_3$ to BNT. It was also observed that the Sm^{3+} derivative has the lowest *Q* values in comparison to compositions with Nd^{3+} and La^{3+}.

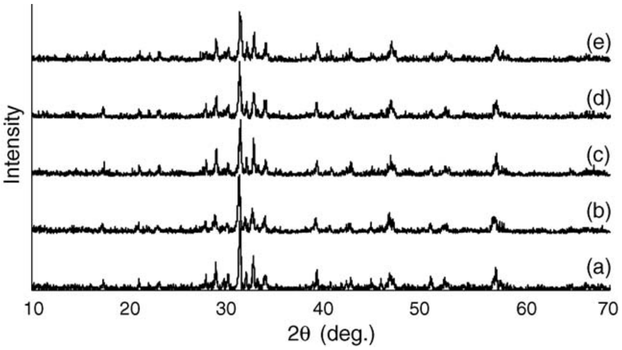

Fig. 3. XRD patterns of BNT sintered at 1340 °C for 2 h with various additions of $NdAlO_3$ where (a) 0 wt.%; (b) 2 wt.%; (c) 5 wt.%; (d) 10 wt.%; and (e) 15 wt.%.

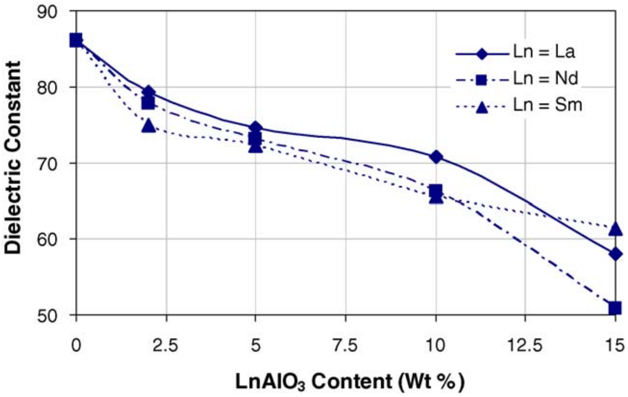

Fig. 4. The change in dielectric constant with addition of $LnAlO_3$ (Ln = La, Nd and Sm) to BNT ceramics sintered at 1340 °C for 2 h.

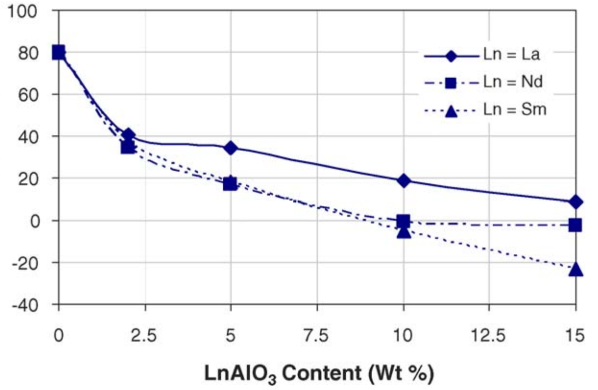

Fig. 5. The change in temperature coefficient of resonant frequency (TC*f*) with addition of $LnAlO_3$ (Ln = La, Nd and Sm) to BNT ceramics sintered at 1340 °C for 2 h.

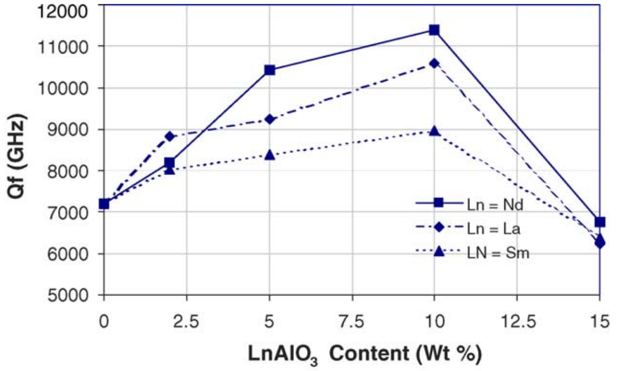

Fig. 6. The change in quality factor (*Qf*) with addition of $LnAlO_3$ (Ln = La, Nd and Sm) to BNT ceramics sintered at 1340 °C for 2 h.

4. Conclusions

The microstructure and dielectric properties of $Ba_{4.2}Nd_{9.2}Ti_{18}O_{54}$ ceramics doped with $LnAlO_3$ (Ln = La, Nd and Sm) have been discussed. Additions of >10 wt.% $NdAlO_3$ diminished grain growth and the densifications process. In addition, typical columnar grain morphology observed in BNT ceramics was transformed to quasi-rectangular shapes accompanied by increase in porosity. XRD analysis did not reveal any second phases or modification of the BNT crystal structure. The relative permittivity and the TC*f* values showed a linear decrease with increasing additions of $LnAlO_3$. It was observed that near zero TC*f* values can be achieved with addition of $LnAlO_3$ dopants to BNT ceramics. On the other hand, the *Q* values exhibited a non-linear behaviour with $LnAlO_3$ additions with maxima attained at approximately 10 wt.% $LnAlO_3$.

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