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Microwave dielectric properties of $(Bi_{1-x}R_x)NbO_4$ ceramics (R = Ce,Nd,Dy,Er)

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Abstract

$(Bi_{1-x}R_x)NbO_4$ (R = Ce,Nd,Dy,Er; $x = 0.03$ mol) ceramics with 0.1 wt.% CuO + V_2O_5 as a sintering aid were prepared by conventional solid state reaction process. The microwave dielectric properties of $(Bi_{1-x}R_x)NbO_4$ ceramics were investigated as a functional of R ions. The microwave dielectric properties such as dielectric constant, Q value and temperature coefficient of resonant frequency (TCF) are found to correlate with the R ions. When R = Ce, the dielectric constant, Q value and TCF are 44.7, 5000 and −4.9 ppm/°C, respectively at about 5 GHz. The relation of microwave dielectric properties and the ionic radii, polarizability and bond valence of R (R = Ce, Nd, Dy, Er) was discussed. The Q value decreased with decreasing the bond valence and the size of R ions. The dielectric constant decreased with decreasing polarizability.

Keywords: Dielectric properties; $BiNbO_4$ ceramic; Sintering; Functional applications; X-ray methods

1. Introduction

The development of dielectric materials for microwave applications has been focused on reducing the size and weight of RF and microwave components in telecommunication. Low temperature co-fired ceramics (LTCCs) have been extensively studied for their applications in multilayer RF and microwave components such as chip LC filter[1] and other planar filter.[2–4] $BiNbO_4$ dielectric ceramics have been proposed as candidate dielectrics for LTCCs due to their low sintering temperatures (<1000 °C) and excellent dielectric properties (ε_r values ~43; Q values ~4000).[5] However, their TCF value is too large (+38 ppm/°C). Several researchers have made efforts to modify the microwave dielectric properties of BiNbO4 ceramics by introducing Nd or Sm substitution for Bi, Ta substitution for Nb.[6–8] It was difficult to densify $BiNbO_4$ without a sintering aid. CuO, V_2O_5 or CuO–V_2O_5 mixtures as a sintering aid used to lower the sintering temperature have been studied in recent years.[9] In this work, R (R = Ce, Nd, Dy, Er) ions were introduced to substitute for Bi ions in the $BiNbO_4$ ceramics. Microwave dielectric properties of $Bi_{1-x}R_xNbO_4$ ($x = 0.03$ mol) ceramics were studied.

2. Experimental procedures

High-purity oxide powders (>99.9%) of Bi_2O_3, Nb_2O_5, and R_2O_3 (R = Ce, Nd, Dy, Er) were used as starting materials. Proportional amounts of starting materials of Bi_2O_3, Nb_2O_5 and R_2O_3, according to the composition of $Bi_{1-x}R_xNbO_4$ ($x = 0.03$), were mixed for 24 h in a nylon jar using ZrO_2 media. Mixed powders were dried and calcined at 800 °C for 2 h and then they were remilled with a small amount of CuO and V_2O_5 mixture (0.1 wt.%) added as a sintering aid. They were pressed into pellets with PVA solution as a binder, and then sintered at about 910–940 °C for 3 h in air. The dimension of the sintered disk was 12 mm in diameter and 6 mm in thickness.

The microstructure observation of the sintered ceramics was preformed by SEM (JOEL, 5510LV). The crystalline phase of sample was identified by XRD (BRUKER, D8). The bulk density of sample was measured by the Archimedes method. The dielectric constant and the quality value Q at approximately 5 GHz were measured using the Hakki-Coleman dielectric resonator methods.[10] The $TE_{01\delta}$ mode was examined using a vector network analyzer (HP8753E). The temperature coefficient of resonant frequency was obtained by measuring $TE_{01\delta}$ resonant frequency at 20 °C and 80 °C, respectively. The temperature coefficient of resonant frequency was defined as following:

$$\mathrm{TCF} = \frac{f_{80} - f_{20}}{60 \times f_{20}} \times 10^6\ (\mathrm{ppm/^\circ C}) \tag{1}$$

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Table 1
Ionic radius, polarizabilities and bond valence parameters of Bi and R (R = Ce, Nd, Dy, Er)

	Ionic radii (Å)	Polarizability	Bond valence parameter
Bi	1.03	6.04	2.094
Ce	1.01	6.01	2.151
Nd	0.983	5.01	2.117
Dy	0.912	4.1	2.036
Er	0.89	3.83	1.988

3. Results and discussions

$(Bi_{1-x}R_x)NbO_4$ (R = Ce, Nd, Dy, Er; $x = 0.03$ mol) ceramics with 0.1 wt.% $CuO–V_2O_5$ addition sintered at 910–940 °C for 3 h exhibited single orthorhombic phase without any second phase determined by XRD except R = Ce. Fifteen percent triclinic phase appeared when R = Ce.[11] But there is small amount triclinic phase in $(Bi_{1-x}Nd_x)NbO_4$ ceramics with 0.5 wt.% $CuO–V_2O_5$ as sintering aid reported by Choi et al.[6] In this case, the amount of sintering aid $CuO–V_2O_5$ is more than 0.1 wt.%, so small amount of orthorhombic phase will transfer to triclinic phase. The density of the samples is 97% of theoretical density.

Ionic radius,[12] polarizabilities[13] and bond valence parameters[14] of Bi and R (R = Ce, Nd, Dy, Er) are listed in Table 1.

The bond valence of atom i, V_i was defined as the sum of all of the valences from a given atom i, and that was calculated in the Eqs. (3) and (4).[14]

$$\nu_{ij} = \exp\left[\frac{(R_{ij} - d_{ij})}{b}\right] \tag{2}$$

$$V_i = \sum_j \nu_{ij} \tag{3}$$

where R_{ij} is the bond valence parameter, d_{ij} the length of a bond between atom i and j, and b is commonly taken to be a universal constant equal to 0.37.

The dielectric constant of $(Bi_{1-x}R_x)NbO_4$ (R = Ce, Nd, Dy, Er; $x = 0.03$ mol) ceramics are showed Fig. 1. The dielectric constant decreased as the R ion changes from Ce to Dy. But when R = Er, the dielectric constant increased. According to the Clausius–Mosotti relation, the dielectric constant of oxide compounds can be calculated as follows.[13]

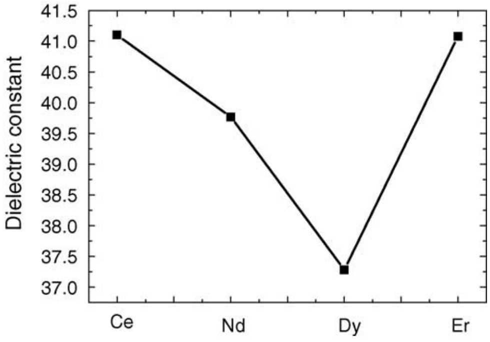

Fig. 1. The dielectric constant as a function of R.

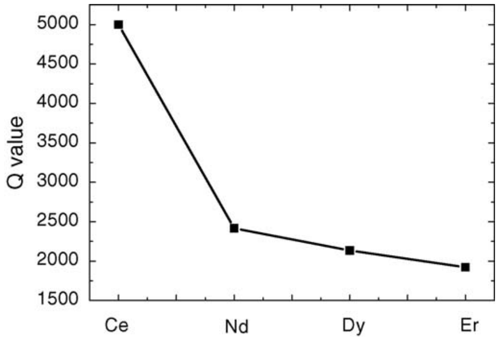

Fig. 2. Q value as a function of R.

$$\varepsilon_r = \frac{3V_m + 8\pi\alpha_D}{3V_m - 4\pi\alpha_D} \tag{4}$$

α_D is the sum of polarizabilities of constituent ions in $(Bi_{1-x}R_x)NbO_4$ and V_m is the molar volume.

The lattice parameters of $(Bi_{1-x}R_x)NbO_4$ ceramics did not change apparently when the content of R is small.[15] According to the Eq. (4), the dielectric constant is mainly determined by α_D. Thus, the decrease in dielectric constant can be ascribed to a decrease in the α_D that decreases with the decreasing of the polarizabilty of the R ions showed in Table 1. But when R = Er, small ionic radii will move easily in oxygen octahedra at an external electrical field. So α_D in Eq. (4) must be corrected when the ionic radii of R is small. On the other hand, A-site bond valence is small when R = Er from Eq. (3) and Table 1. A-site Er^{3+} ion behaved like the rattling cation, which resulted in higher dielectric constant.

Fig. 2 showed Q value decreased when the substitute of A-site ion was Ce, Nd, Dy and Er, respectively. The size difference of ionic radii such as Bi and R increase as R = Ce, Nd, Dy and Er. The Q value decreased with the increase of the size difference between Bi and R. A-site bond valence in Eqs. (2) and (3), neglecting the change of lattice parameters, decreased when the R ion changes from Ce to Er. The stabilization of structure decreases when the bond valence decreases. There was no change in microstructure observed,[11] thus the decrease in Q value can result from a decrease in the stabilization of structure.[16] The Ce-compound has better Q value than other compounds. A phase transformation (orthorhombic to triclinic) occurred as R = Ce. About 15% triclinic phase appeared in Ce-compound.[11] The appropriate triclinic phase resulting in higher Q values was reported in other $BiNbO_4$ based ceramics.[6]

Fig. 3 showed the TCF value with various R ions. The TCF value decrease as the R ion changes from Nd to Er. The Ce-compound may be related to triclinic phase. In this case, that exhibits the microwave dielectric constant 41.58, the quality value (Q) value 5000 (at 5.4 GHz) and TCF value −4.9 ppm/°C. As TCF value obey the additional rule, a material with TCF = 0 ppm/°C can be easily obtained.

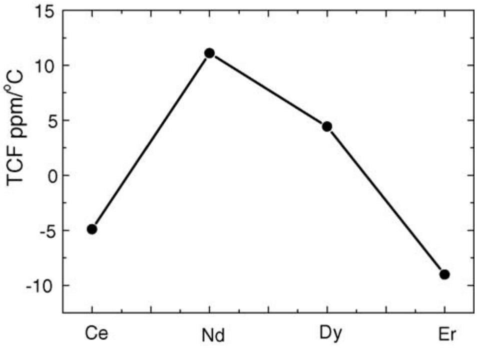

Fig. 3. TCF value as a function of R.

4. Conclusions

The microwave properties of $(Bi_{1-x}R_x)NbO_4$ (R = Ce,Nd, Dy,Er; $x = 0.03$ mol) ceramics were examined. The dielectric constant decreased as the R ion changes from Ce to Dy. Because of small size and bond valence, the dielectric constant increased when R = Er. The *Q* value of $(Bi_{1-x}R_x)NbO_4$ ceramics decreased as the R ion changes from Ce to Er. This tendency is the same as A-site bond valence. The TCF value decreased as the R ion changes from Nd to Dy. When R = Ce, the quality factor (*Q*) value is 5000 (at 5.4 GHz) and TCF value −4.9 ppm/°C.

Acknowledgements

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