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Effect of dopants on microwave dielectric properties of $Ba(Zn_{1/3}Nb_{2/3})O_3$ ceramics

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Abstract

$Ba(Zn_{1/3}Nb_{2/3})O_3$ (BZN) has been prepared with various amounts of different dopants such as oxides of monovalent, divalent, trivalent, tetravalent, pentavalent and hexavalent elements. Effect of these dopants on microwave dielectric properties of BZN is investigated. Some of the dopants are found to increase quality factor Q × f and slightly alter the temperature coefficient of resonant frequency (τ_f). Annealing undoped BZN increased the quality factor. Small amounts of dopants such as oxides of Ni, In, Al, Ga, Zr, Ce, Sn, Ti, Sb, and W increased the quality factor. The doped ions substitute for the ordered B ions decreasing the order parameter. Annealing increased the quality factor for all doped BZN samples. Doping BZN with In_2O_3, Al_2O_3, WO_3 and SnO_2 decreased the order parameter but at the same time increased the quality factor indicating that order parameter alone is a poor indicator of quality factor. The quality factor is found to depend on the dopant ionic radii and its concentration. The quality factor increased when the ionic radius of the dopant is close to the ionic radius of the B site ions Zn or Nb. Microstructure studies using SEM showed that the doped high Q ceramics contained large grains.

Keyword: Powders-solid state reaction; Calcination; Sintering; Dielectric properties; Niobates

1. Introduction

$Ba(Zn_{1/3}Nb_{2/3})O_3$ [BZN] is a well known microwave dielectric resonator material with a perovskite cubic structure[1] with dielectric constant $\varepsilon_r = 41$, quality factor Q × f = 33,000 and temperature coefficient of resonant frequency $\tau_f = +28$ ppm/°C. As-prepared BZN has a disordered cubic symmetry with Zn and Nb ions occupying B sites in a random way. On prolonged heating the structure becomes partially ordered perovskite structure with Zn–Nb–Nb repeat sequence along the ⟨1 1 1⟩ direction of the parent cubic perovskite cell.[1,2] Kim et al.[2,3] studied the ordering in $Ba(Ni_{1/3}Nb_{2/3})O_3$ and $Ba(Zn_{1/3}Nb_{2/3})O_3$ using XRD and Raman Spectroscopy. It was reported[3] that the $Ba(Ni_{1/3}Nb_{2/3})O_3$ samples sintered at 1400 °C for 2 h were disordered and showed presence of Nb rich liquid phase at grain boundary junctions. Degree of ordering increased with annealing at 1300 °C. Ordering in solid solutions of composition $(1-x)Ba(Zn_{1/3}Nb_{2/3})O_3$–$xLa(Zn_{1/3}Nb_{2/3})O_3$, $0.0 \le x < 0.6$ were studied by Akbas and Davies.[4] They observed that the stability of trigonal 1:2 ordered structure of the $Ba(Zn_{1/3}Nb_{2/3})O_3$ end member is very limited and low levels of lanthanum induce a transformation to cubic 1:1 ordered structure. Similar results showing the presence of 1:1 ordering of BZN were also reported by Barbar et al.[5]

It is common to make solid solution of BZN with other perovskite materials like $Sr(Zn_{1/3}Nb_{2/3})O_3$, $Ba(Ni_{1/3}Nb_{2/3})O_3$, $Ba(Co_{1/3}Nb_{2/3})O_3$,[1,3,4,6] etc. to tune temperature coefficient of resonant frequency to a value near to zero and to improve microwave dielectric properties. Dielectric behavior and structure of $Ba_xSr_{1-x}(Zn_{1/3}Nb_{2/3})O_3$ solid solution were investigated by Colla et al.[6] and established a correlation between τ_ε and O-octahedral tilts. Colla et al. established[7] the presence of ferroelastic domains and studied their influence on τ_ε. Microwave dielectric properties of $Ba(Sn_xZn_{(1-x)/3}Nb_{(1-x)2/3})O_3$ was investigated by Sun et al.[8] for values of $0 \le x \le 0.32$. They could obtain a zero τ_f material for 22.6 mol% Sn addition. Dielectric properties of $0.95Ba(Zn_{1/3}Nb_{2/3})O_3$–$0.05BaZrO_3$ were investigated by Huang et al.[9] They obtained a dielectric constant $\varepsilon_r = 40$–41, quality factor Q × f = 15,000–96,000 GHz and $\tau_f = +27$ ppm/°C for $0.95Ba(Zn_{1/3}Nb_{2/3})O_3$–0.05 $BaZrO_3$ ceramics sintered at 1450 °C for 2 h.

Dopants like Sb_2O_3 and B_2O_3 were added to $Ba[(Ni_{0.6}Zn_{0.4})_{0..33}Nb_{0.67}]O_3$ to reduce the sintering temperature from 1550 to 1330 °C.[10] Thus in the forgoing several mechanisms like

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increase in density, grain growth, volatilization of Zn and stabilization of ordering domain boundaries have been proposed to explain the increase in microwave dielectric properties of BZN. A recent study[11] on the effect of dopants on microwave dielectric properties of $Ba(Zn_{1/3}Ta_{2/3})O_3$ has revealed that the improvement in quality factor takes place when the ionic radius of the dopant becomes close to the ionic radii of the B site ions Zn and Ta. Hence we have doped BZN with different dopants such as oxides of, monovalent element like Li, divalent elements like Mg, Ni, trivalent elements like Al, Cr, In, Bi, Ga, tetravalent elements like Zr, Ce, Sn, Ti, pentavalent element Sb and hexavalent element like W to study their effects on microwave dielectric properties and to understand the mechanism of enhancement in the quality factor and other microwave dielectric properties of $Ba(Zn_{1/3}Nb_{2/3})O_3$.

2. Experimental

BZN was synthesized using conventional solid-state ceramic route. Powders of 99.9% pure $BaCO_3$, ZnO (Aldrich chemical company) and Nb_2O_5 (NFC, India) were weighed in stoichiometric proportion and were mixed well in distilled water medium in a plastic container. Zirconia balls were added to the plastic container and ball milled for 24 h. The slurry was dried and powdered in an agate mortar and calcined at 1200 °C in air for 4 h. The calcination temperature and duration was optimized for the best quality factor. Necessary predetermined quantities of dopants in the form of oxides (Aldrich chemical company) were added to the calcined powder and again ground well in an agate mortar for about 1 h and the binder (4 wt% poly vinyl alcohol) was added. The slurry was mixed well, dried and reground in an agate mortar for 1 h before pressing in a die into pellets of approximate size of 15 mm diameter and 7 mm height. These pellets were sintered in a high temperature furnace. The sintering temperature and duration were optimized for the best quality factor. After sintering the samples were cooled at a rate of 2°/min until 1000 °C and a cooling rate of 8 °C/min was given to reach room temperature. The pellets were powdered to record X-ray diffraction pattern using Cu Kα radiation. Sintered samples were polished well to remove surface irregularities and were used for measuring microwave dielectric properties. The bulk densities of the samples were measured using Archimedes method. Sintered samples of BZN were annealed at 1250 °C for different durations. Duration of annealing was optimized for the best quality factor and was found to vary from dopant to dopant. Optimized annealing conditions were determined for each dopant.

The microwave dielectric properties of the samples were measured using HP 8510B Net Work Analyzer in the frequency range 3–6 GHz. The TE_{011} mode was used for all the measurements. The dielectric constant (ε_r) was measured by the Hakki and Coleman[12,13] method and the quality factor ($Q \times f$) was measured by the cavity method.[14] By heating the sample and noting the variation of the resonant frequency, temperature variation of the resonant frequency (τ_f) was determined. The sintered samples were fractured and the surfaces were subjected to SEM analysis to observe differences between microstructures of the doped and undoped BZN.

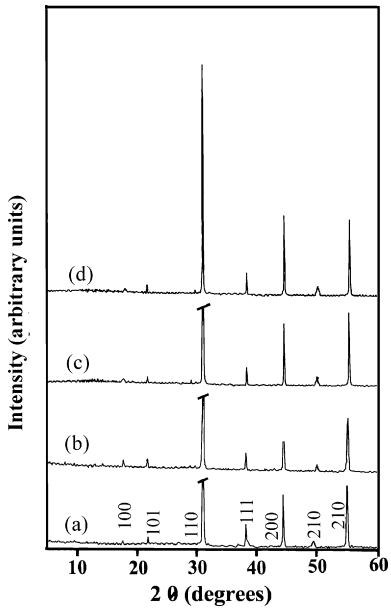

Fig. 1. XRD patterns (using Cu Kα radiation) (a) pure BZN in as sintered condition, (b) pure BZN in sintered and annealed for 10 h at 1250 °C, (c) doped BZN with 1 mol% of WO_3 (sintered and annealed), (d) doped BZN with 1 mol% of SnO_2 (sintered and annealed). Superlattice reflection is 1 0 0 peak which is strongest for (b) and weakest for (a).

3. Results and discussion

X-ray diffraction study showed the formation of phase pure BZN after synthesis and the XRD patterns shown in Fig. 1 were in agreement with the JCPDS data file No. 17-182. Doping did not produce any additional peaks on the XRD pattern indicating the absence of secondary phases. Calcination and sintering conditions of BZN was optimized for the best quality factor. Fig. 2 shows the variation of density and quality factor $Q \times f$ with calcination temperature and Fig. 3 shows variation of $Q \times f$ with calcination duration (for samples sintered at 1450 °C for 4 h). The density and quality factor increased with increase in calcination and reached a maximum at 1200 °C. On further increase in calcination temperature decreased the density and quality factor. Hence the optimized calcination temperature is 1200 °C.

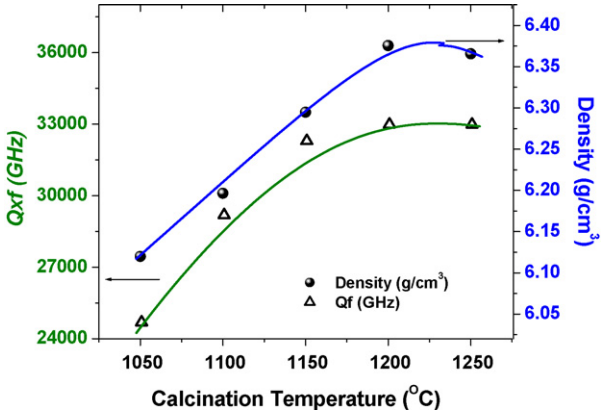

Fig. 2. Variation of density and $Q \times f$ with calcination temperature for undoped BZN (calcination duration 4 h). The samples were sintered at 1450 °C for 4 h.

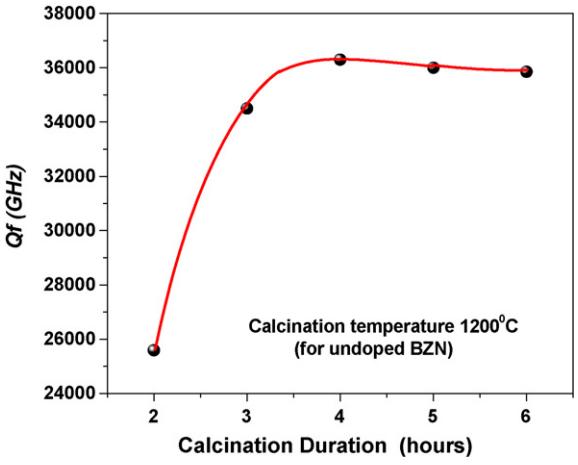

Fig. 3. Variation of Q × f with calcination duration for undoped BZN. The samples were calcined at 1200 °C and sintered at 1450 °C for 4 h.

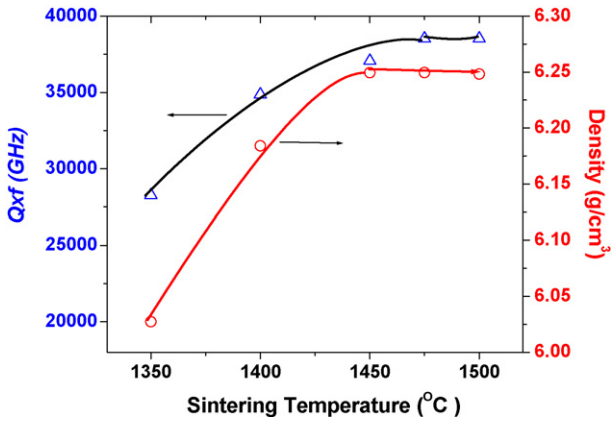

Fig. 4. Variation of density and Q × f with sintering temperature for undoped BZN (calcined at 1200 °C, 4 h).

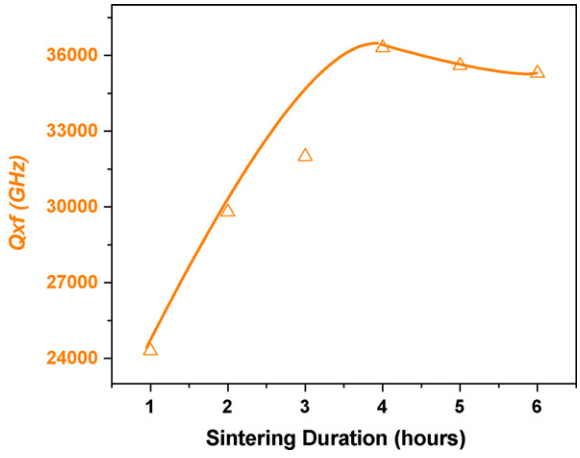

Fig. 5. Variation of Q × f with sintering duration of undoped BZN.

The Q × f increased with calcination duration and reached a maximum for 4 h at 1200 °C. Hence the optimized calcination conditions for undoped BZN were found to be 1200 °C for 4 h. The density and Q × f increased with increase in sintering temperatures up to 1450 °C and then remained almost constant (see Fig. 4). Fig. 5 shows the variation of quality factor (Q × f) with sintering duration. It is clear from Fig. 5 that maximum Q × f was obtained when the samples were sintered for 4 h at 1450 °C. Hence the optimized sintering conditions for undoped BZN were 1450 °C for 4 h. The undoped BZN sintered up to 96% of the theoretical density. The quality factor increased with an increase in annealing duration at 1250 °C. The Q × f reached a maximum when annealed for 10 h for undoped BZN. Further annealing decreased Q × f. Fig. 6 shows the variation of quality factor (Q × f) for undoped BZN samples annealed at 1250 °C for different annealing durations. The as sintered BZN had dielectric constant $\varepsilon_r = 39$, quality factor Q × f = 37,600 GHz and $\tau_f = 27$ ppm/°C. On annealing at 1250 °C for 10 h Q × f was found to increase to 48,600 GHz without much variation in ε_r and τ_f (Table 1 and Fig. 6). However a decrease in Q × f was noticed on further annealing. Similar reduction in Q × f with sintering temperature was observed for $Ba(Zn_{1/3}Ta_{2/3})O_3$.[11,15,16] Tables 1 and 2 and Figs. 7–10 show the effect of addition of the

Table 1
Effect of 0.5 mol% dopant addition on properties of BZN

Dopant and stable valency	Ionic radius (AU) (Shannon)[16]	Annealing time for attaining best properties (h)	% Density	Q × f GHz before annealing	Q × f GHz after annealing (1325 °C)	τ_f (ppm/°C)	ε_r
Pure BZN	–	10	96.9	37,600	48,600	27.0	39.0
$Al^{(3+)}$	0.535	5	97.4	69,400	77,400	29.1	40.2
$W^{(6+)}$	0.6	10	96.0	58,300	80,500	33.5	37.9
$Ti^{(4+)}$	0.61	5	95.1	61,300	67,800	28.7	39.7
$Cr^{(3+)}$	0.615	5	92.5	39,600	68,000	26.7	38.1
$Ga^{(3+)}$	0.62	10	94.6	32,000	65,300	27.4	39.7
$Co^{(2+)}$	0.65	10	94.9	30,000	41,600	31.9	39.7
$Mn^{(4+)}$	0.67	5	95.2	40,300	41,000	29.9	42.6
$Sn^{(4+)}$	0.69	10	96.0	37,300	69,000	27.9	39.6
$Ni^{(2+)}$	0.69	10	96.8	48,500	67,000	27.7	42.3
$Mg^{(2+)}$	0.72	10	96.9	40,750	46,000	31.9	41.7
$Zr^{(4+)}$	0.72	10	95.5	55,250	83,680	26.9	39.4
$Sb^{(5+)}$	0.74	25	93.0	11,400	65,900	28.2	39.2
$Li^{(1+)}$	0.76	5	93.7	8,500	11,200	29.7	41.9
$In^{(3+)}$	0.8	10	94.3	56,900	65,800	27.7	40.6
$Ce^{(4+)}$	0.87	10	96.2	36,100	69,000	40.2	40.1

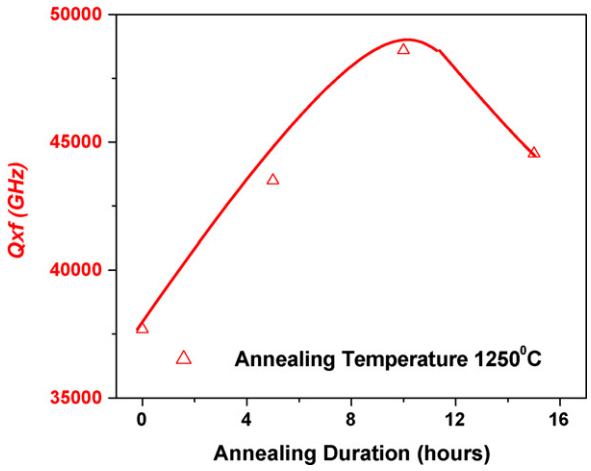

Fig. 6. Variation of Q × f with annealing duration of undoped BZN (annealing temperature 1250 °C).

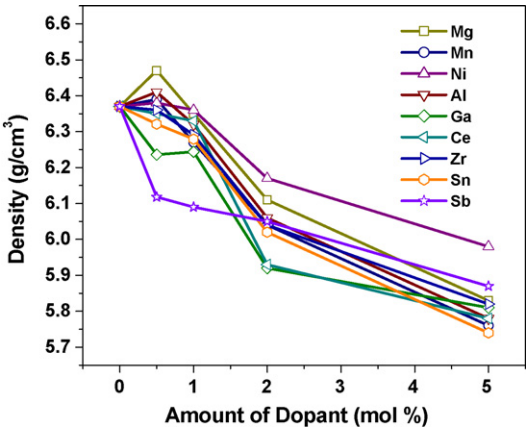

Fig. 7. Variation of density with amount of dopants for BZN.

different dopants, with different valences and ionic radii, on the microwave dielectric properties of BZN. Tables 1 and 2 also show the Q × f of the doped samples before and after annealing at 1250 °C. The annealing times given in the tables were for obtaining the maximum quality factor and it varies from dopant to dopant. Addition of small amounts of dopants improves

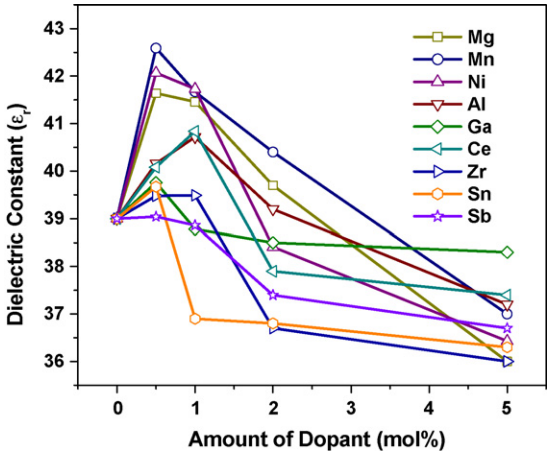

Fig. 8. Variation of dielectric constant with amount of dopants for BZN.

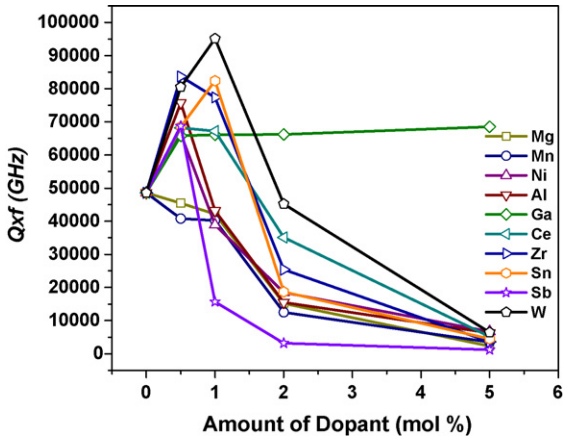

Fig. 9. Variation of quality factor (Q × f) with amount of dopants for BZN.

densification. However if the amount of dopants are more, it will result in a reduction in density due to formation of second phases as can be seen in Fig. 2. Addition of 0.5 mol% divalent dopant NiO, trivalent dopants like In_2O_3 and Al_2O_3, tetravalent dopants like GaO_2, ZrO_2, CeO_2, SnO_2 and TiO_2, pentavalent dopant Sb_2O_5, and hexavalent dopant like WO_3 are found to improve Q × f. With increase in the amount of dopants to 1 mol%, only SnO_2 and WO_3 show further increase in Q × f value while other dopants are found to deteriorate the Q × f. Doping 2 or more mol% always deteriorate the quality factor except for gallium oxide. The highest Q × f of 95,100 GHz was observed for samples doped with 1 mol% WO_3 (Q × f = 95,100) and SnO_2 (Q × f = 83,200) followed by 0.5 mol% doping with ZrO_2 (Q × f = 83,600), WO_3 (Q × f = 80,500), In_2O_3 (Q × f = 79,300) and Al_2O_3 (Q × f = 77,400). The τ_f in general is increased by the dopant addition except for Zr and Cr for which slight decrease in τ_f was noticed. It is also observed that the doping does not considerably alter the dielectric constant of BZN. In general dielectric constant is slightly increased by the addition of dopants up to 0.5 mol% and decreased on further doping.

It was observed that an annealing treatment given to BZN after the sintering has improved the microwave quality factor considerably for most of the dopants. This improvement is

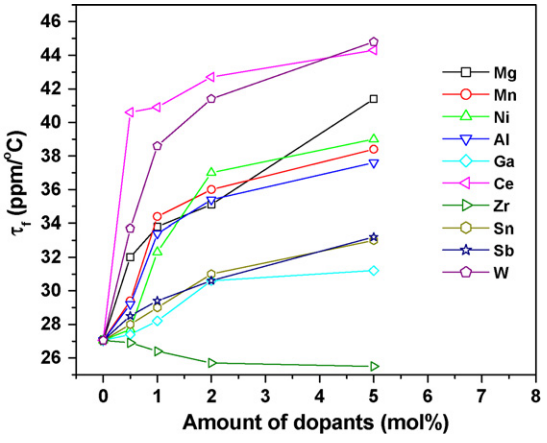

Fig. 10. Variation of temperature coefficient of resonant frequency with amount of dopants for BZN.

Table 2
Effect of 1 mol% dopant addition on properties of BZN

Dopant and stable valency	% Density	Annealing time (h)	Q × f GHz before annealing	Q × f GHz after annealing	τ_f (ppm/°C)	ε_r
Pure BZN	96.9	10	37,600	48,600	27.0	39.0
$Al^{(3+)}$	96.0	5	44,600	43,000	33.1	40.7
$W^{(6+)}$	93.0	5	80,870	95,150	38.7	38.4
$Ti^{(4+)}$	93.7	25	32,300	45,750	30.9	39.1
$Cr^{(3+)}$	91.6	20	17,300	25,300	26.8	39.2
$Ga^{(3+)}$	94.9	20	33,500	68,000	27.8	39.8
$Co^{(2+)}$	94.9	5	15,000	17,300	31.6	39.9
$Mn^{(4+)}$	97.1	10	36,000	40,000	33.4	41.6
$Sn^{(4+)}$	95.2	10	62,200	83,200	29.0	36.8
$Ni^{(2+)}$	96.7	5	35,000	41,000	32.3	41.7
$Mg^{(2+)}$	96.5	10	33,000	42,000	33.6	41.4
$Zr^{(4+)}$	95.6	10	55,600	77,800	26.2	40.3
$Sb^{(5+)}$	92.3	5	9,975	15,000	29.2	38.8
$Li^{(1+)}$	93.0	5	No resonance	–	–	–
$In^{(3+)}$	92.8	5	No resonance			
$Ce^{(4+)}$	96.5	10	57,400	69,500	40.9	41.0

attributed to the 1:2 ordering of Zn and Nb ions (Zn–Nb–Nb) on the B site.[2] Some of the doped samples showed improved Q × f values on annealing and the increase in Q × f is found to vary differently for different dopants. To study the degree of ordering on Q × f, order parameter *S* was calculated for several high Q × f samples using X-ray diffraction techniques. The long – range order parameter *S* is defined as[3]

$$S = \sqrt{\frac{[I_{100}/I_{110,102}]_{obs}}{[I_{100}/I_{110,102}]_{calculated}}}$$

where $[I_{100}/I_{110}]_{obs}$ is observed and $[I_{100}/I_{110}]_{calculated}$ is the calculated relative integrated intensities.

Calculated order parameter values of annealed pure BZN and those doped with 0.5 mol% In_2O_3, Al_2O_3 and with 1 mol% SnO_2 and WO_3 are given in Table 3. The order parameter of undoped BZN increases on annealing. However doping BZN with In_2O_3, Al_2O_3, WO_3 and SnO_2 decreases the order parameter but at the same time the quality factor is increased. The doped ions are expected to substitute partially for ordered B-ions. The effect of dopant was not taken into account in calculating diffracted intensity. Hence probably doping may not decrease the ordering but may decrease only the order parameter.

Fig. 11 shows the variation Q × f of BZN with ionic radius of the dopant for 0.5 and 1 mol% dopant additions. It can be seen from Fig. 11 that Q × f shows a maximum when the ionic radii of the dopant is close to the ionic radii of the B site ions Zn or Nb. It is evident from Fig. 11 that Q × f increases when the ionic radii of the dopant is close to 0.64 and 0.74 which are the ionic radii of Nb and Zn, respectively. W and Ga have ionic radii 0.6 and 0.62 which are near to that of Nb. Zr, Sn and In have ionic radii 0.72, 0.69, 0.8 which are close to that of Zn. These dopants increase the quality factor considerably. Exception to this observation was found for indium and cerium which has ionic radius 0.8 and 0.87 which are away from the ionic radius 0.74 of Zn and still have high quality factor. A similar observation was reported by Varma et al.[11] in BZT for which Q × f increases when the ionic radii of the dopant is close to 0.64 and 0.74 which are the ionic radii of Ta and Zn, respectively. Surendran et al.[17,18] observed that in the case $Ba(Mg_{1/3}Ta_{2/3})O_3$ [BMT] dopants with ionic radii close to 0.65 increase the quality factor. In BMT dopants with ionic radii in the range 0.6–0.7 increase the quality factor. These values are close to the weighted average ionic radius of [1/3Mg + 2/3Ta] which is 0.653.

Table 3
Order parameters of pure and doped BZN under different heat treatment conditions

Condition of the material	Order parameter
Undoped BZN (as sintered)	0.74
Undoped BZN (sintered and annealed)	0.88
BZN + 0.5 mol In_2O_3 (sintered and annealed)	0.83
BZN + 1 mol WO_3 (sintered and annealed)	0.84
BZN + 0.5 mol Al_2O_3 (sintered and annealed)	0.82
BZN + 1 mol SnO_2 (sintered and annealed)	0.84

SEM analysis of fractured surfaces of undoped BZN and that doped with 0.5 mol% Li_2O and 1 mol% ZrO_2, Ga_2O_3 and WO_3 is shown in Fig. 12. It can be seen (Fig. 12(a)) that the undoped BZN had large grains of approximate grain area of

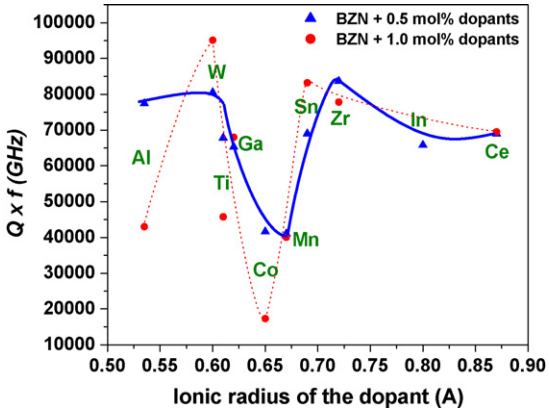

Fig. 11. Variation of Q × f with ionic radius of dopant for 1 and 0.5 mol% dopant addition in BZN.

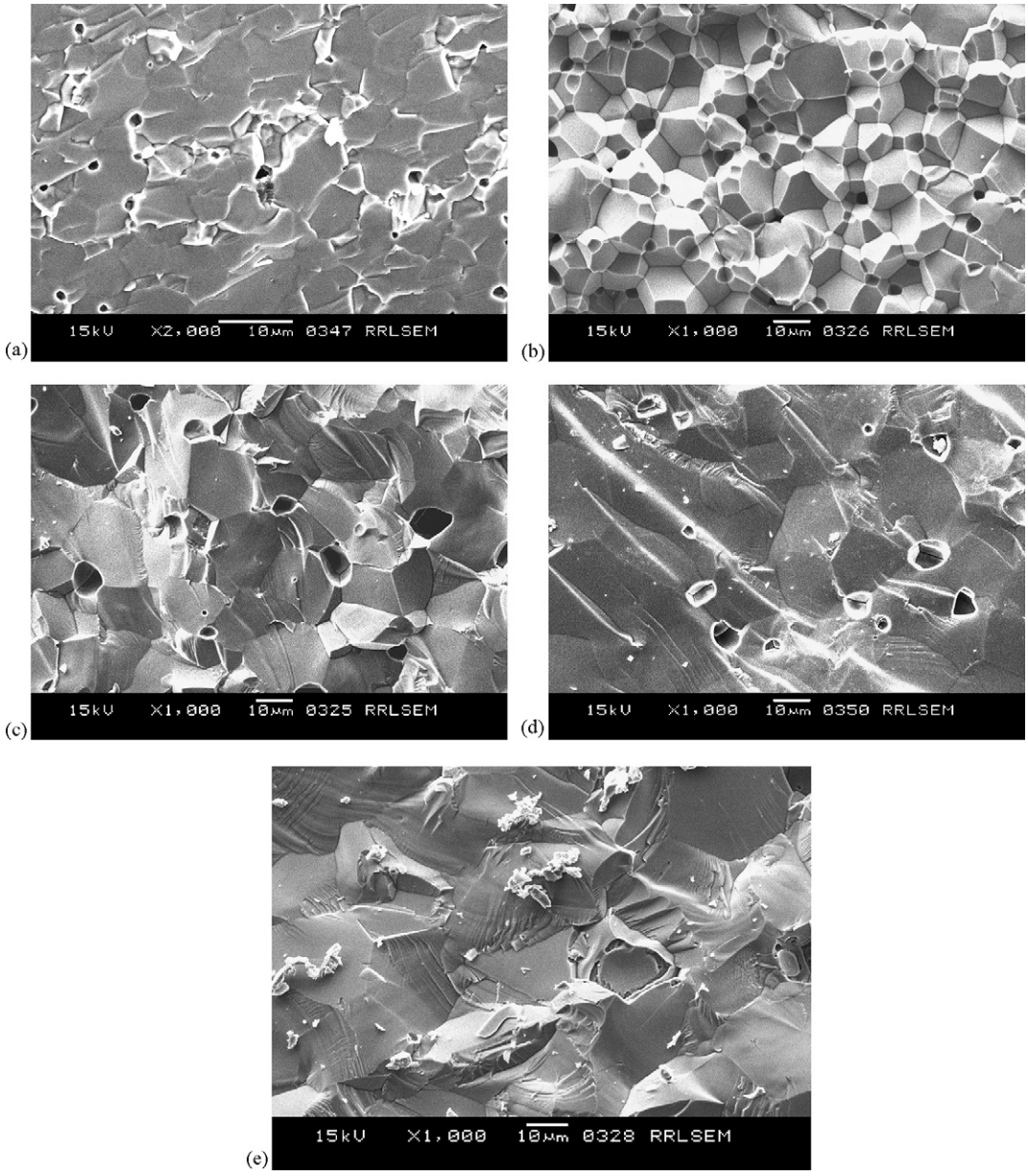

Fig. 12. SEM micrographs of BZN: (a) undoped, (b) doped with 0.5 mol% Li_2O, (c) doped with 1 mol% ZrO_2, (d) doped with 1 mol% Ga_2O_3 and (e) 1 mol% WO_3.

about 39 μm^2 which is reduced to about 34 μm^2 (Fig. 12(b)) when 0.5 mol% Li was added. However, addition of oxides of Zr, Ga and W has resulted in considerable grain growth as can be seen in Fig. 12(c)–(e). Average grain size are increased to about 166 μm^2 for ZrO_2, 225 μm^2 for Ga_2O_3 and 214 μm^2 for WO_3. Hence it appears that dopants with ionic radius close to the B site ions are found to be promoting grain growth and improves microwave dielectric properties of sintered BZN.

4. Conclusions

Addition of 0.5 mol% dopants NiO, In_2O_3, Al_2O_3, Ga_2O_3, ZrO_2, CeO_2, SnO_2, TiO_2, Sb_2O_3, and WO_3 is found to improve the quality factor in BZN with relatively small changes in τ_f and ε_r. When the amount of dopants were increased to 1 mol%, $Q \times f$ was found to increase for dopants SnO_2 and WO_3, while other dopants are found to decrease the $Q \times f$. Doping 2 or more mol% always deteriorate the quality factor. The quality factor increases when the ionic radius of the dopant is close to the ionic radii of the B site ions Zn and Nb. Microstructure studies using SEM indicate that the ceramics with high Q have large grains.

Acknowledgement

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