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Effect of V_2O_5 on the sintering behaviour, cation order and properties of $Ba_3Co_{0.7}Zn_{0.3}Nb_2O_9$ ceramics

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Abstract

The microstructures and microwave dielectric properties of barium cobalt zinc niobate ceramics prepared by conventional mixed oxide route have been investigated. It was found that low level doping of V_2O_5 (up to 0.2 wt.%) could significantly improve densification of the specimens and their microwave dielectric properties. Dielectric properties of V_2O_5 doped samples were affected by 1:2 ordering in the B-site. Slow cooling after sintering or annealing in nitrogen atmosphere improved the unloaded quality factor (Q.f values) significantly. The $Ba_3Co_{0.7}Zn_{0.3}Nb_2O_9$ (BCZN) ceramics exhibited $\varepsilon_r = 34.5$, $\tau_f = 0$ ppm/C and Q.f = 85,000 at 4 GHz.
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1. Introduction

Ceramic dielectrics have been extensively used for microwave communication systems. The advantage of using microwave dielectric ceramics is the size reduction of microwave components. Requirements for these dielectric materials must be the combined dielectric properties of a high dielectric constant (ε_r), low dielectric loss (high Q.f value) and a near-zero temperature coefficient of resonant frequency (τ_f). These three parameters related to the size, frequency selectivity and temperature stability of the system, respectively. To satisfy the demands of microwave circuit designs, each dielectric property should be precisely controlled. Several complex perovskites ceramics $A(B'_{1/3}B''_{2/3})O_3$ have been known for their excellent microwave dielectric properties. Among these materials, $Ba_3Co_{0.7}Zn_{0.3}Nb_2O_9$ possesses a high dielectric constant ($\varepsilon_r \sim 34.5$), a high quality factor (Q.f 56,000–85,000 GHz) and small temperature coefficient of resonant frequency ($\tau_f \sim 0$).[1–3]

In this study, we investigate the effect of V_2O_5 on the sintering behaviour, cation order and microwave dielectric properties, particularly the Q.f values of $Ba_3Co_{0.7}Zn_{0.3}Nb_2O_9$ ceramics.

2. Experimental

Specimens were prepared by a conventional mixed oxide route. High purity(>99.9%) $BaCO_3$, ZnO, Nb_2O_5 and V_2O_5 were used as raw materials. The powders were weighed according to the composition $Ba_3Co_{0.7}Zn_{0.3}Nb_2O_9$ + 7.5 wt.% $Ba_8Zn_1Nb_6O_{24}$. They were mixed in propan-2-ol with zirconia media for 18 h, calcined at 1100 °C for 4 h, then V_2O_5 was added and wet milled for 18 h and dried. Pellets were formed by pressing powders in steel dies (20 mm diameter) at a pressure of 100 MPa. These were sintered at 1450 °C for 4 h in air and cooled at 60 °C/h. Selected compositions were annealed in nitrogen atmosphere at 1360 °C for up to 10 h. The final dimensions of these specimens were approximately 15.5 mm diameter and 9 mm thick.

Microstructural observation of the sintered ceramics was performed by means of SEM (Philips XL30). The sintered surfaces of ceramics were ground (to 1200 grade SiC) and polished (to 1 μm diamond paste). The samples were then coated with carbon prior to SEM analysis.

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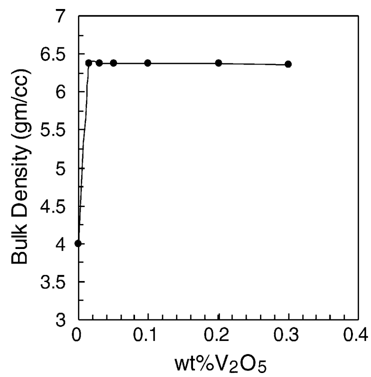

Fig. 1. Bulk densities of BCZN ceramics as a function of V_2O_5 content.

The crystal structures were examined by XRD (Philips Analytical, X'pert-MPD) employing Cu Kα1 radiation under the conditions 50 kV and 40 mA. The samples were scanned at 0.04° intervals of 2θ in the range 10–70°; the scan rate was 0.01°2θ/s.

TEM specimens were prepared from the sintered ceramics, after lapping and polishing to form 3 mm diameter discs. The discs were dimpled to 30 μm thickness in the centre and then thinned to electron transparency with a Gatan Precision Ion Polishing System. The specimens were investigated using a Tecnai G2 operating at 300 kV.

The dielectric properties were measured by parallel plate method.[4] The τ_f measurements were performed using a silver plated aluminium cavity at temperatures between −10 and +60 °C.

3. Results

Fig. 1 shows the bulk densities of BCZN ceramics. It can be seen that the addition of V_2O_5 promoted densification. A similar trend was observed for the Q.f values of the samples as shown in Fig. 2. Fig. 3 shows the XRD spectrum of samples prepared with 0.025 wt.% V_2O_5. The pattern shows the characteristics of a 1:2 ordered hexagonal structure with the presence of the superstructure reflection at $2\theta = 17.6$. An extra peak was observed at $2\theta = 29.6°$ which is associated with the formation of the $Ba_8Zn_1Nb_6O_{24}$ phase.

The increase in the Q.f values is a result of combined effect of the increase in density, structural homogenisation in atomic levels and Zn, Co and Nb ordering on the B-sites, which are achieved by a liquid phase mechanism through the additions of vanadium oxide.

The dielectric constants and τ_f values of the dense samples were not significantly affected by V_2O_5 additions and

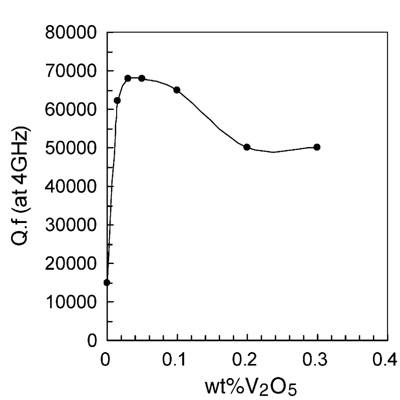

Fig. 2. Q.f values of BCZN ceramics a function of V_2O_5 content.

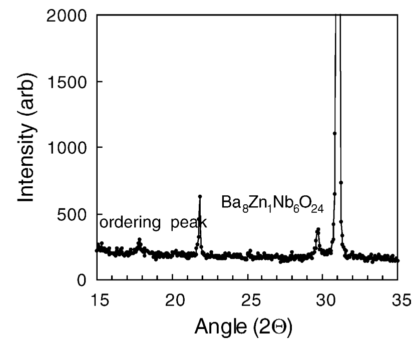

Fig. 3. Typical XRD spectrum of the BCZN ceramics.

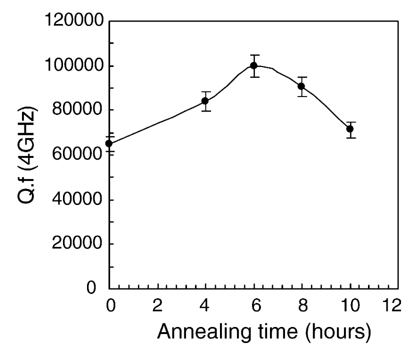

Fig. 4. Q.f values as function of annealing time.

Fig. 5. TEM image of BCZN ceramics.

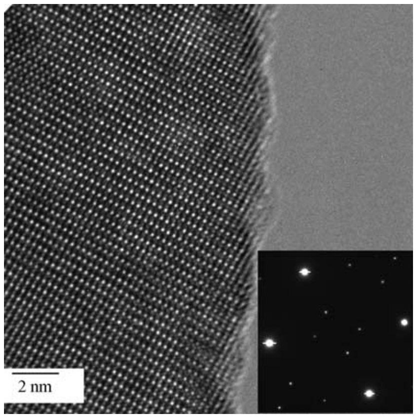

Fig. 6. High-resolution TEM image of BCZN ceramics.

were ∼34.5 and ∼0 ppm/°C, respectively. Further enhancement of the quality factor of the ceramics was achieved by annealing in nitrogen atmosphere at temperatures below the order-disorder transition (Fig. 4). XRD examinations showed that the increase in the degree of B-site ordering is a main factor for the enhancement in the Q.f values.

The formation of the $Ba_8Zn_1Nb_6O_{24}$ phase was confirmed by SEM and TEM examination. Fig. 5 shows bright field TEM image of the above sample. The $Ba_8Zn_1Nb_6O_{24}$ phase appeared as elongated needle shape grains in the microstructure. The presence of structural modulations can be seen in the grains of this phase. This phase was observed at the grain boundaries as well as within BCZN grains. Fig. 6 shows high resolution TEM image of a single domain. The grain viewed along ⟨0 1 1⟩ type zone axis of the cubic unit cell.

4. Conclusions

High density with high degree of 1:2 order BCZN ceramics were achieved by additions of vanadium oxide. BCZN ceramics with 0.025 wt.% V_2O_5 addition sintered at 1450 °C for 4 h and annealed in nitrogen atmosphere possessed excellent microwave dielectric properties: $\varepsilon_r \sim 34.5$, Q.f value ∼85,000 at 4 GHz and τ_f of close to 0.

Acknowledgements

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