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Development of low cost, high performance $Ba(Zn_{1/3}Nb_{2/3}O_3)$ based materials for microwave resonator applications

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Abstract

Solid solutions of the $(x)Ba(Zn_{1/3}Nb_{2/3})O_3$ – $(1\text{-}x)Ba(Co_{1/3}Nb_{2/3})O_3$ system were produced by the mixed oxide route. Sintering temperatures of 1300–1500 °C with cooling rates of 3–180 °C/h were used. Sintered densities of $\leqslant 95\%$ were achieved. A second phase deficient in Co and Zn was detected. Slow cooling after sintering, down to 900 °C, induced B-site ordering which increased the dielectric Q values. Compositions near to $0.6[Ba(Zn_{1/3}Nb_{2/3})O_3]$ – $0.4[Ba(Co_{1/3}Nb_{2/3})O_3]$ exhibited zero temperature dependence of resonant frequency ($\tau_f \sim 0$). The presence of the second phase (Zn/Co deficient) improved the dielectric properties. Ceramics of optimum composition, having $x \sim 0.6$, have excellent electrical properties, (Q value $\sim$43,000 at 2 GHz, relative permittivity $\varepsilon_r \sim 35.5$ and τ_f tunable through zero). The material will offer a new design option for filter engineers in the development of 3G and other similar telecommunication systems.

Keywords: Dielectric resonators; $Ba(Zn,Nb)O_3$; Resonators; Microwave ceramics; Mobile telecommunications

1. Introduction

Microwave dielectric ceramics are utilized in both mobile telecommunication handsets and base station filtering technologies. Other systems such as GPS antennas also require this type of low loss ceramic. There are three major electrical properties that microwave dielectric ceramics must address, ε_r (relative permittivity), Q (Quality factor $\sim 1/\tan\delta$) and τ_f (temperature co-efficient of resonant frequency). The non linearity co-efficient (NLC) is also important for design purposes; this is a measure of the linearity of τ_f as a function of temperature.

Ceramic components can offer improved performance compared to conventional air cavity filter systems. In addition to being physically smaller, microwave dielectrics also allow more users for a given bandwidth; power handling is improved giving a better signal to noise ratio. However, cost can become a major factor when choosing microwave dielectrics for filter applications.

$Ba(Zn_{1/3}Ta_{2/3})O_3$ (BZT) has been a popular high performance ($\varepsilon_r \sim 30$, Q$\sim$55 k at 2 GHz) temperature stabilized material, available to filter engineers. However the high cost (related to the cost of Ta_2O_5) lowers its cost effectiveness for many applications. It has therefore become necessary to develop microwave dielectrics with similar performance to BZT but at a much reduced cost. In recent years there has been considerable interest in the development of a $Ba(Zn_{1/3}Nb_{2/3})O_3$ (BZN) based system.[1]

Onoda et al.[2] and Endo et al.[3] respectively investigated the effects of mixed Ba/Sr and Zn/Co sites in BZN and highlighted the versatility and tuning capabilities of the BZN system. Recent work by Reaney et al.,[4] based on analysis of the tolerance factor suggested that the Zn/Co route would give the best opportunity for a high Q, temperature stabilized material. They suggested that a reduction of the range of ionic radii in the crystal structure would help to reduce the lattice strain. This reduction in strain is likely to help lower the dielectric loss of the sintered ceramic. Several authors discuss the importance of B-site ordering for optimizing the electrical properties of BZN type ceramics. Davies et al.[5] described the change in crystal structure from the disordered (Pm3m) cubic array to the trigonal (P3m1) ordered unit under the correct conditions. The fact that ordering could be affected by the use of modifiers such as $BaZrO_3$ and $Ba(Ga_{1/2}Ta_{1/2})O_3$ has also been examined, especially in $Ba(Zn_{1/3}Ta_{2/3})O_3$ (BZT) ceramics.[6] Hughes

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et al.[7] explored the BZCN system in a recent paper which highlighted that commercial products were feasible in an optimized material. However, this work did not suggest the formation of an ordered superstructure when analysed by X-ray diffraction (XRD). This indicated that ordering is not the only critical parameter for the production of high Q dielectrics from this type of complex perovskite.

The present study addressed the development of $Ba[(Zn/Co)_{1/3}Nb_{2/3})]O_3$ (BZCN) based materials.

2. Experimental

High purity (>99.9%) oxides and carbonates were used for the preparation of powder formulations in the BZCN system. Standard aqueous ball milling (~75% solids content) using 1/4″ ZrO_2 media was used during the powder manufacture. Calcination schedules ranging from 1000 to 1350 °C and 2–20 h in air were performed on the powder samples. These were uniaxially pressed (to ~65% of fired density) and sintered at a variety of regimes from 1300–1500 °C for 2–100 h in air or nitrogen. Cooling rates of 180–3 °C/h were used on the sintered samples to maximize the electrical properties.

Fired sample densities were determined by a water immersion technique. XRD analysis was performed using a Philips PW1830 diffractometer, operated at 40 kV and 40 mA with a 0–70° 2θ range. SEM investigations were completed on a Topcon ABT-60 operating at 15 kV, combined with a PGT Prism XDS system for chemical analysis. Surface and cross section samples were produced; both were carbon coated. Sectioned samples were polished to 1 μm finish; no etchants were used.

Microwave measurements were performed in transmission mode, using a Wiltron 37247B Vector Network Analyzer. Sample size was, on average ~1/3 cavity diameter and ~1/8 cavity height. ε_r and τ_f measurements were carried out at 8GHz. Parallel plates were used for the determination of ε_r whilst τ_f was measured in an appropriate cavity within a gas controlled temperature cabinet over a 70 to −30 °C temperature range.

3. Results and discussion

The fired density for a well sintered sample exhibiting τ_f ~0 was approximately 6.4 gcm^{-3}, although this could be altered according to the levels of second phase produced during sintering. XRD analysis of the production material highlighted the presence of additional peaks on the spectra for calcined powder. In addition to the strong simple cubic peaks of the perovskite phase, super lattice reflections and second phase peaks were also identified (Fig. 1). The powder exhibits a peak for barium niobate, or chemically similar second phase second phase peak

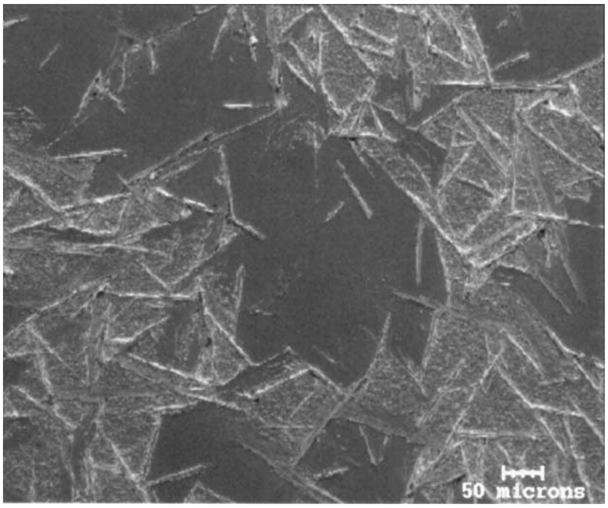

Fig. 2. SEM micrograph of the as-fired surface of a doped BZCN sample, sintered at 1375 °C 10 h.

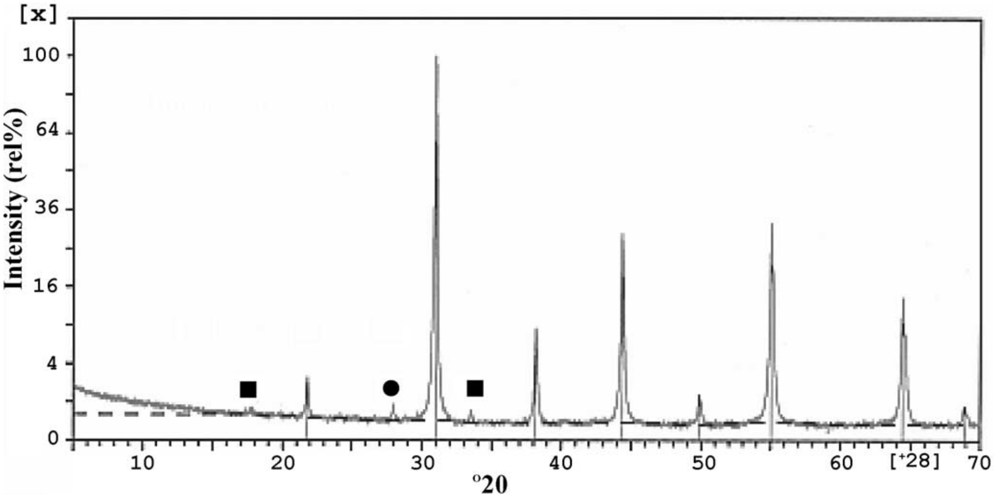

Fig. 1. XRD spectrum from a doped BZCN powder, calcined at 1200 °C for 10 h in air (Barium niobate peak (●); B-site ordering peaks (■)).

(~28°2θ) and additional ordering peaks (~17.5°2θ and ~33°2θ). These peaks are also present in slow cooled (<20 °C/h) sintered ceramics.

The barium niobate (BN) phase was detected on the surface of sintered samples, and traces were also found internally. Figs. 2 and 3 show growth of BN on the as-fired surface and the growth of the striations into the ceramic bulk respectively. These phases were identified by EDS as containing less Zn and Co than the surrounding ceramic. The formation of the barium niobate phase is thought to occur in a similar way to the formation of barium tantalate (BT) in BZT ceramics. The effect of the surface chemistry is not as well understood in BZN. However in BZT, the volatilization of Zn from the surface of the sample during sintering (~1500 °C) gives rise to a phase close to a Ba–Ta binary. The varying stoichiometry of this phase causes large changes in measured Q values in BZT, and similar effects are expected in BZCN. Removal of the surface layer (containing the second phase), via sample grinding, lowered the Q of the samples substantially. It is concluded that the growth of the BN type phase is initiated on the sample surface via Zn/Co volatalisation, which then continues to propagate into the material bulk during the sintering process (Fig. 3).

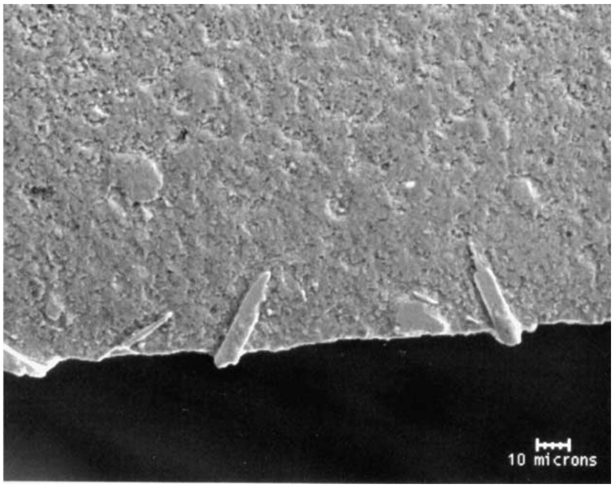

Fig. 3. SEM micrograph of polished BZCN sample showing growth of second phase into the ceramic body.

Crystallographic ordering of the B-site cations in repeat layers can dramatically affect the Q values of some perovskite structure microwave dielectrics. In BZN ordering normally occurs as either 1:1, with a complete Nb layer followed by a layer of mixed Nb and Zn/Co ions, or 1:2 where there are two repeat layers of Nb for every one of Zn/Co. These arrangements can be altered however, by the addition of modifiers such $BaZrO_3$ (BZ) and $Ba(Ga_{1/2}Ta_{1/2})O_3$ (BGT). Hong et al.[8] discussed the formation range of these ordered ceramics and the requirement to sinter within the ordered range for extended periods to maximize ordering. Davies et al.[9] discussed the effect of ordering on the Q value of a sintered ceramic, showing that ordering can be important in dielectric property development. The thermodynamic driving force for such ordering is low in BZT

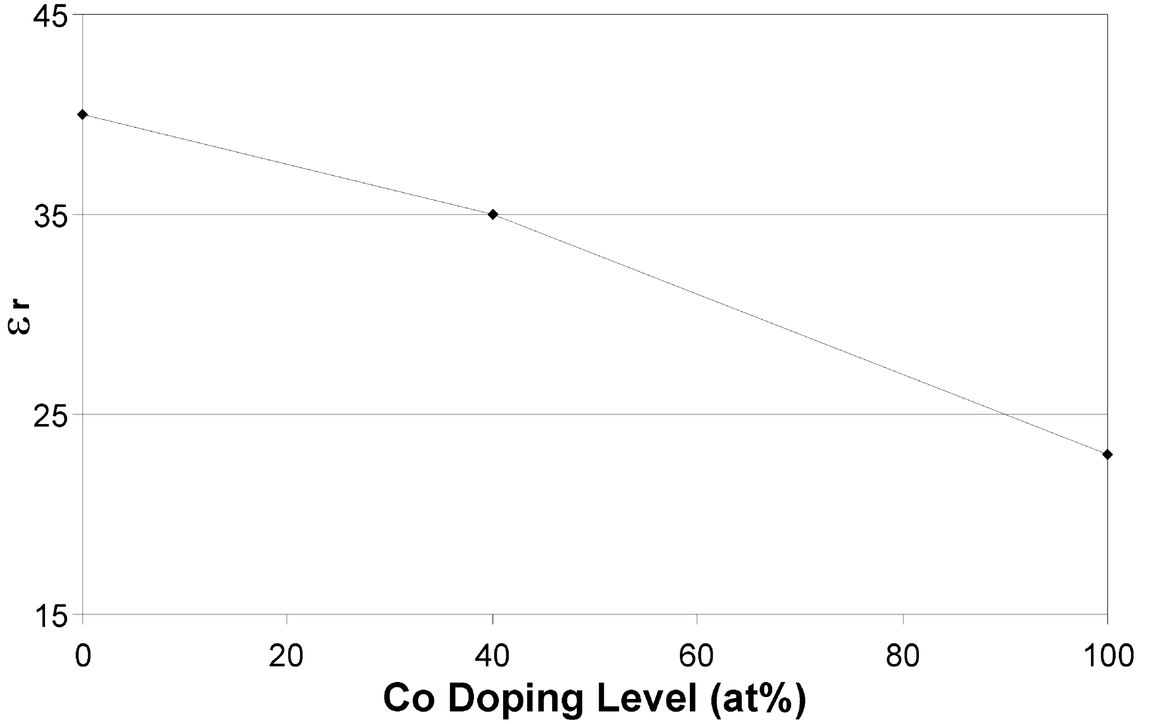

Fig. 4. ε_r values as a function of Co substitution for Zn in the $Ba(Zn_{1/3}Nb_{2/3})O_3$–$Ba(Co_{1/3}Nb_{2/3})O_3$ system.

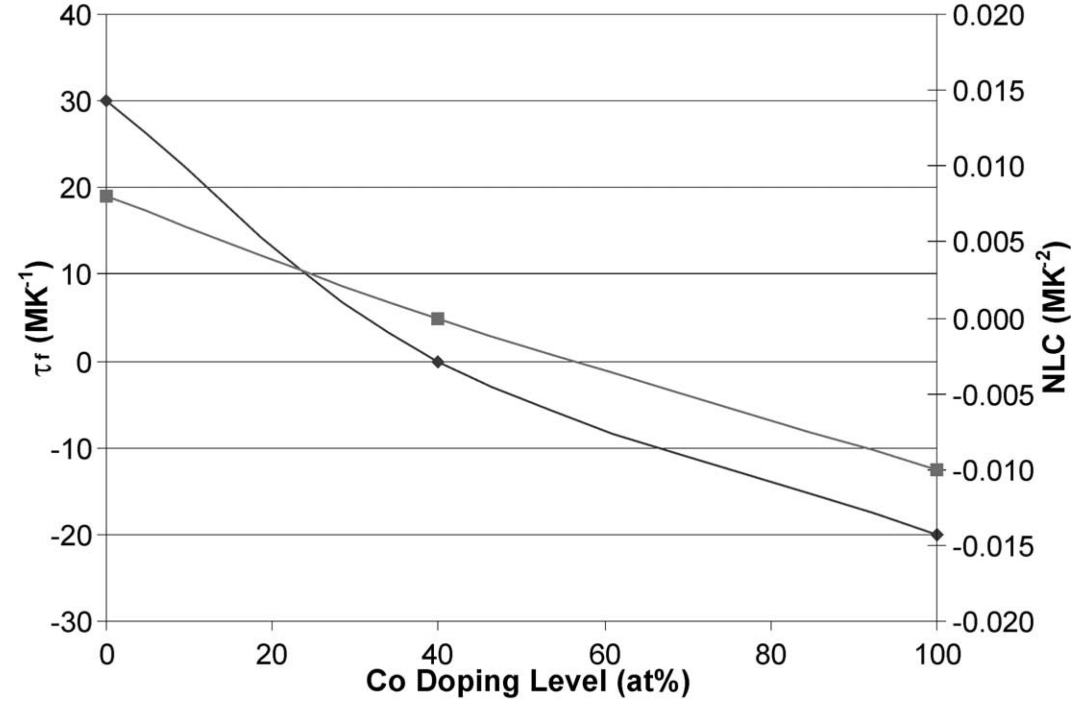

Fig. 5. τ_f (◆) and NLC (■) values as a function of Co substitution for Zn in the $Ba(Zn_{1/3}Nb_{2/3})O_3$–$Ba(Co_{1/3}Nb_{2/3})O_3$ system.

Table 1
Q values at 2 GHz for BZCN samples prepared using different cooling regimes after sintering

Cooling rate (°C/h)	Final temperature for slow cooling regime (°C)		
	1100	1000	900
3	38,000	41,000	43,000
5	36,000	–	–
10	32,000	38,000	40,000

and even lower in BZN with the lower processing temperatures giving slower kinetics.

Figs. 4 and 5, show the decrease in both ε_r and τ_f as the Co^{2+} concentration on the Zn^{2+} site was increased. Product development concentrated on the near zero τ_f region of Fig. 5 (~60% Zn^{2+}), with subsequent investigations focused on optimization of the electrical properties at this composition.

Q_o values of ~30,000 at 2 GHz could be produced using rapid sintering schedules (~100 °C/h). However,

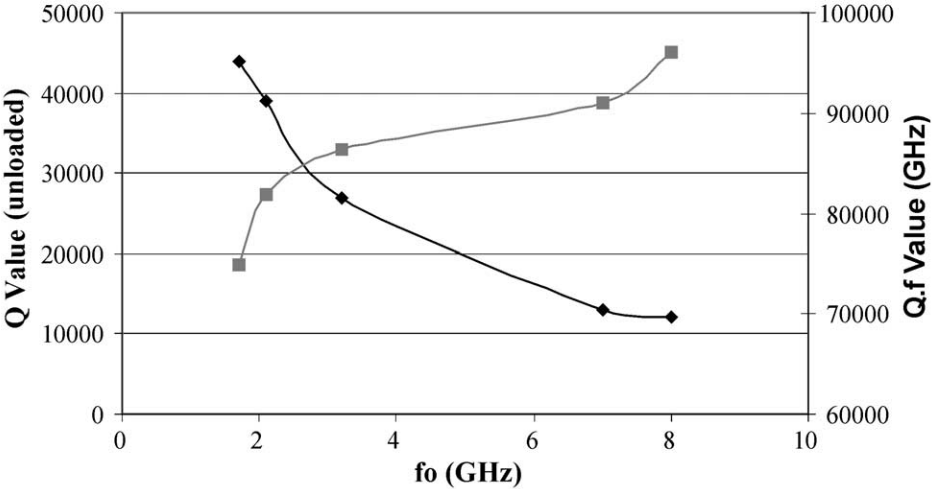

Fig. 6. Q (◆) and Q.f (■) values for BZCN as a function of frequency.

Q_o (unloaded Q) values were improved by up to 25% by slow cooling (~5 °C/h) the samples through the critical order-disorder region. This region was found to occur between 1100 and 1250 °C for a $\tau_f = 0$ MK^{-1} doped composition. Further improvements were found by continuing the slow cooling to lower temperatures, although the mechanism is not yet understood. Table 1 highlights the change in Q value achievable by control of the cooling methodology.

Dielectric properties were measured over a range of frequencies to assess the overall performance of the material. Fig. 6 shows the change in Q as a function of sample frequency (size); all samples were sintered at 1400 °C for 10 h with a 5 °C/h cooling rate to 900 °C.

The next phase of the study will examine the effects of processing and site stoichiometry on electrical properties of BZCN. This work will include the determination of a phase diagram for the BZCN system and a study of second phase formation and its effect on the dielectric properties.

Trials based on 2GHz resonator pucks (Ø ~28 mm, I.D~10 mm, t ~12 mm) have yielded Q values in excess of 42,000. Initial analysis suggests the cost for a 2 GHz resonator, produced in BZCN will be around 50% of that of an equivalent BZT puck.

4. Conclusions

Using the mixed oxide route good quality ceramics of $0.6[Ba(Zn_{1/3}Nb_{2/3})O_3]$–$0.4[Ba(Co_{1/3}Nb_{2/3})O_3]$ have been prepared which exhibit industrially relevant properties, (Q_o ~43,000 at 2 GHz, ε_r ~35.5 and $\tau_{f=}0\pm3$ MK^{-1}). Slow cooling of the ceramic through the order-disorder region was the greatest influence on promoting high Q values in the samples. The formation of a Zn/Co deficient second phase, both on the surface and in the bulk are thought to be beneficial to final electrical properties.

BZCN ceramics will offer a high Q solution for base station filtering at a greatly reduced cost compared to BZT ceramics.

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