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Structure and dielectric properties of perovskite ceramics in the system $Ba(Ni_{1/3}Nb_{2/3})O_3$–$Ba(Zn_{1/3}Nb_{2/3})O_3$

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Abstract

Ceramics in the system $Ba(Ni_{1/3}Nb_{2/3})O_3$–$Ba(Zn_{1/3}Nb_{2/3})O_3$ (BNN–BZN) were prepared by the mixed oxide route. Powders were mixed and milled, calcined at 1100–1200 °C then pressed and sintered at temperatures in the range 1400–1500 °C for 4 h. Selected samples were annealed or slowly cooled after sintering. Most products were in excess of 96% theoretical density. X-ray diffraction confirmed that all specimens were ordered to some degree and could be indexed to hexagonal geometry. Microstructural analysis confirmed the presence of phases related to $Ba_5Nb_4O_{15}$ and $Ba_8Zn_1Nb_6O_{24}$ at the surfaces of the samples. The end members BNN and BZN exhibited good dielectric properties with quality factor (Qf) values in excess of 25,000 and 50,000 GHz, respectively, after rapid cooling at 240 °C h^{-1}. In contrast, mid-range compositions had poor Qf values, less than 10,000 GHz. However, after sintering at 1450 °C for 4 h and annealing at 1300 °C for 72 h, specimens of $0.35(Ba(Ni_{1/3}Nb_{2/3})O_3)$–$0.65(Ba(Zn_{1/3}Nb_{2/3})O_3)$ exhibit good dielectric properties: τ_f of +0.6 ppm °C^{-1}, relative permittivity of 35 and quality factor in excess of 25,000 GHz. The improvement in properties after annealing is primarily due to an increase in homogeneity.

Keywords: Dielectric properties; Perovskites; Niobates

1. Introduction

Complex perovskite dielectric ceramics are good candidate materials for microwave frequency applications. Ta-based systems, such as $Ba(Zn_{1/3}Ta_{2/3})O_3$ (BZT) and $Ba(Mn_{1/3}Ta_{2/3})O_3$ (BMT) are widely used due to their high relative permittivity (ε_r), quality factor (Qf) and low temperature coefficient of resonant frequency (τ_f).[1,2] The high cost of Ta oxides has called for research of other similar, low-cost materials, such as analogous Nb-based systems.

$Ba(Ni_{1/3}Nb_{2/3})O_3$ and $Ba(Zn_{1/3}Nb_{2/3})O_3$ are cubic perovskite ceramics with spacegroup P_{m3m}. The ordered form of the material introduces lower symmetry, and the system can be indexed as a hexagonal structure (spacegroup P_{-3m1}). A transition from the ordered to the disordered state has been observed in BNN at temperatures above 1400 °C[3–8] and in BZN at above 1300 °C.[6,9] The majority of the previous studies attribute this to the formation of a liquid phase at the grain boundary at and above the transition temperature. As a result, defect concentrations in the grain boundaries are higher, resulting in disorder in the lattice. The order–disorder transitions were found to be coincident with transitions in the lattice parameters. The amount of secondary phase increases with sintering temperature, and also with sintering time above 1500 °C, signifying an increase in the extent of liquid-phase formation during sintering. The increase in the amount of liquid phase and subsequent lattice imperfections at higher temperatures reduces the degree of ordering. In contrast, where homogeneous calcined powders have been used, liquid-phase sintering does not occur and the degree of ordering increases with increasing sintering temperature.[3] However, it has been shown that remnants of this liquid phase, which remains as an intergranular second phase, can dissolve back into the primary material during annealing.[10] Some investigations have also identified NiO-based inclusions in BNN due to unreacted starting materials, emphasising the importance of ensuring homogeneity after calcination.

These findings are consistent with other studies that have taken a “first principles” approach to predicting the order–disorder transition.[11,12] However, the calculated transition temperatures are higher than the experimentally determined values. This difference was attributed to the inability of the theoretical model to account for inhomogeneity and liquid-phase sintering. Noh et al.[13] showed that the quality factor increases with sintering temperature and time up to the transition temperature,

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although the degree of ordering did not vary significantly. The large improvements seen in Qf values have been attributed to the higher densities and larger grain sizes brought about by liquid-phase sintering.[13]

The high volatility of Zn and Ni introduces further complications. The longer sintering and/or annealing times required to improve the degree of ordering encourage the loss of these species from the material during processing. This leads to a surface region rich in barium niobate.[14]

In the system BNN–BZN, compositions with τ_f of (or near) zero can be achieved, but sometimes at the cost of other properties. Ceramics of 0.7BNN–0.3BZN sintered at 1500 °C have been reported to have a zero temperature coefficient of resonant frequency with an acceptably high quality factor.[15] However, this does not give the highest possible Qf value. As with the majority of perovskite ceramics, small variations in the processing condition have marked effects on the properties. The temperature-stable composition can vary depending on the processing conditions. For example, Lee et al.[16] prepared a 0.4BNN–0.6BZN composition with a zero τ_f. This apparent discrepancy can be attributed to variations in the processing routes, as well as the nature of the starting materials and the homogeneity of the sintered products.

The focus of the present study is the $Ba(Ni_{1/3}Nb_{2/3})O_3$–$Ba(Zn_{1/3}Nb_{2/3})O_3$ system. The effect of the processing route on the physical and dielectric properties has been investigated, addressing in particular, the sintering temperatures, cooling rates and annealing times, with a view to producing a temperature-stable material with a high relative permittivity and Qf, suitable for use as a low-cost microwave dielectric ceramic.

2. Experimental

Samples were produced via the mixed-oxide route. High purity oxides $BaCO_3$, NiO, ZnO and Nb_2O_5 were mixed in appropriate proportions and vibro-milled with propan-2-ol and zirconia milling media for 24 h (B_2O_3 was added to BNN to improve sinterability). After drying, the powders were calcined at 1100–1200 °C for 4 h, then milled as before and dried. Batches of powder (10 g) were uniaxially pressed in a steel die to form disc-shaped pellets. For sintering, the samples were placed on powder of the same composition on an alumina plate and covered with an alumina crucible to minimise loss of volatile species. Sintering was performed in a Vecstar VF1 chamber furnace at temperatures in the range 1400–1500 °C for 4 h. Standard heating and cooling rates were 240 °C h^{-1}. Selected samples were cooled at slower rates (down to 2 °C h^{-1}) and annealed at 1300 °C for times up to 72 h. Fired densities were determined from weight and dimension measurements.

Sintered samples were ground on SiC down to 1200 grade and polished using 6 and 1 μm diamond paste. A thermal etch at 1100 °C was sufficient to reveal the microstructure. The samples were examined using a Phillips XL30 FEG scanning electron microscope. A Philips SEM525 EDAX DX4 scanning electron microscope was used for EDX analysis. For X-ray diffraction analysis, polished and as-sintered samples were cut to size using a diamond-tipped saw and then examined by a Philips PW1877 employing Cu Kα1 radiation. Samples were scanned from 10 to 110° 2θ in a continuous mode at 0.008° 2θ s^{-1}. Lattice parameters were derived from the diffraction data. The degree of ordering was determined by comparing the hexagonal (1 0 0) peak to the (1 1 0, 0 1 2, 1 0 2) peak. Dielectric loss and relative permittivity were determined by the Hakki-Coleman (parallel plate) method[17] in association with an HP 8720ET network analyser. The temperature coefficient of resonant frequency (τ_f) was determined using a silver-plated aluminium cavity over the temperature range −10 to 60 °C.

3. Results and discussion

From Fig. 1 it can be seen that density generally increases with increasing sintering temperature. This is attributed primarily to the increased level of diffusion at high temperatures. For BZN, maximum density was achieved at sintering temperatures of 1450–1475 °C, whilst for the other end member, BNN, the optimum sintering temperature was 1475 °C. At these temperatures, densities in excess of 96% theoretical were achieved. Reducing the cooling rate after sintering from 240 to 2 °C h^{-1} caused nonlinear variation in density (Fig. 2). For both BZN and BNN the density initially reduced as cooling rate became slower, but there was a slight increase in density for cooling rates in the range 30–10 °C h^{-1} (Fig. 2). This was followed by a reduction

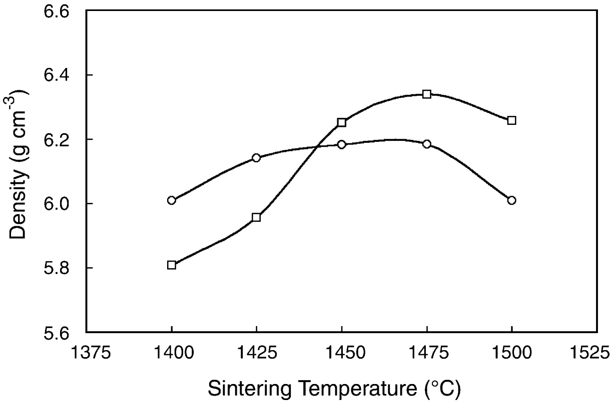

Fig. 1. Density as a function of sintering temperature for BNN (□) and BZN (○).

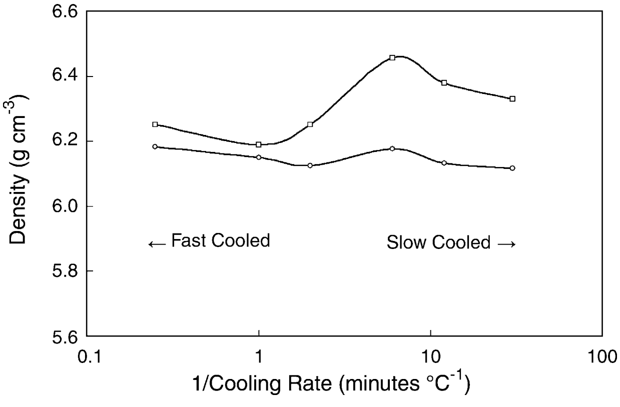

Fig. 2. Density as a function of postsinter cooling rate for BNN (□) and BZN (○).