

High temperature synthesis of barium Zinc Niobate with flux

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Abstract

The complex perovskite oxide $\text{Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (BZN) have been widely studied due to its attractive dielectric properties which place this material as a good candidate for manufacturing type I capacitors or hyperfrequency resonators. The processing conditions *e.g.* soaking temperature and time, amount of flux, and composition of the flux influence the properties and dielectric parameters of the materials. Formation of secondary phase occurs at high calcinations range of temperatures (beyond 1300°C). BZN is extensively employed in microwave communications. The single phase BZN can be successfully prepared by using NaCl + KCl flux at a wide range of temperatures. The phase compatibility, growth of particle size and difference in microstructures have been explained on the basis of powder XRD analyses and Scanning Electron Micrographs (SEM) images of the calcined samples.

Keywords: Dielectric materials, BZN, Flux, XRD, SEM

Introduction

Due to low dielectric losses, associated with a temperature stable permittivity and a high insulating resistivity, the complex perovskite oxide $\text{Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ are compatible for manufacturing type I dielectric applications. Unfortunately, BZN requires a high temperature (1350 °C according to the literature) to reach a satisfactory density (>90% of the theoretical one) [1-3]. That is too high to envisage a silver co-sintering ($T_{f(\text{Ag})} = 961$ °C). For this reason, the lowering of the sintering temperature has been investigated. In the recent years, increasing demand of higher frequency (> 10GHz) for communication systems requires materials with higher Q . The perovskites $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$ (BZT), $\text{Ba}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$ (BMT), $\text{Ba}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (BMN), and $\text{Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (BZN) show good microwave dielectric properties [4-6].

Although tantalate high Q perovskites such as $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$ (BZT), and $\text{Ba}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$ (BMT), have been commercialized, in the last few years, economic factors associated with the high cost of Ta_2O_5 have increased the focus on their niobate counterparts like BMN and BZN as prospective candidates to substitute expensive tantalate perovskite like BZT and BMT. The BZN exhibits a lower T_s (1350 °C) and good dielectric properties ($\epsilon_r = 41$, $\tau_f = 30$ ppm/°C, $Q \times f = 54$ THz at 10 GHz) [7]. However, the resonance frequency temperature coefficient (τ_f) of the BZN ceramic is relatively high (30 ppm/°C), and this limits BZN ceramics also to be used in microwave applications.⁸ These oxides are normally prepared by the solid state route at high temperatures of 1100 °C and are further sintered at 1350–1500 °C for optimum dielectric properties. The solid state route, however, has the disadvantages of high calcinations and sintering temperatures as well as formation of strongly agglomerated particles which may affect the properties of the final product [9]. So, there is an increasing demand to discover alternate routes of synthesis by using flux (Molten Salt Synthesis-MSS) method [10, 11]. Grain size being the crucial factor for higher Q values [12] attempts were made to achieve *grain growth* applying different processing methods and

conditions. In MSS grain size depends on the initial time period of flux treatment [10]. The Q factor of the stoichiometric BZN strongly depends on the density and grain size not on the crystal structural order. The ceramic microstructure such as the pore and grain boundary, the secondary phase and lattice defect caused by non-stoichiometry affect the variation of the Q factor in BZN system than the crystal-structural ordering [13]. In the case of BZN much higher Q factor was found in the disordered phase sintered below 1350°C than the ordered-phase sintered above 1350 °C [14].

This paper explains the influences of processing parameters such as soaking temperature and time, amount of flux, and composition of the flux on the formation mechanism, and on the morphological properties of the BZN powders. Characterization of the materials and study of the effect of calcinations on the phase stability and microstructure have been done by powder XRD and SEM studies

Experimental Procedure

The starting materials were BaCO_3 (99+% Sigma Aldrich, USA), ZnO (99+% Sigma Aldrich, USA), and Nb_2O_5 (99.5% Alfa aesar, UK). Various batches of samples of BZN composition with flux (Equimolar NaCl + KCl) were prepared. The samples were ground in acetone for 1h using Agate mortar- pestle to obtain homogeneous mixtures and then calcined at 1200 °C-1400 °C for different durations (Table 1). The materials, after calcinations on attaining room temperature, were washed with hot distilled water several times until the filtrate gave no precipitate with AgNO_3 . The powders were then dried and subjected to characterizations. Powder XRD of different samples undergone calcinations at various temperatures and durations were carried out (Fig.1-3) and the samples were further examined (Fig 4-6) by using Field Emission Scanning Electron Microscopy (FESEM).

Table1: Samples compositions and processing summary

Samples with flux	Calcinations
N	1200 °C/3h
O	1200 °C/6h
P	1200 °C/10h
Q	1250 °C/10h
R	1300 °C/3h
S	1300 °C/10h
T	1350 °C/3h
U	1350 °C/10h
V	1370 °C/10h
W	1390 °C/10h
X	1400 °C/6h

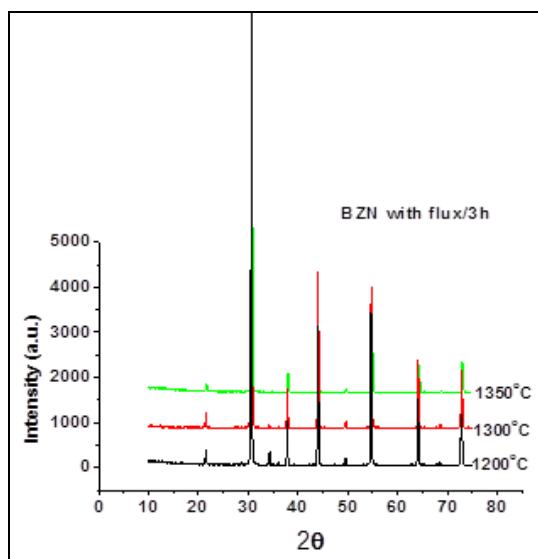


Fig 1: Powder XRD patterns of BZN with flux samples calcined at 1200 °C- 1350 °C for 3hrs.

The fig. 1 shows PXR patterns of the three samples with flux calcined for 3hrs at 1200-1350 °C. It can be seen that all these samples crystallize in a pure perovskite phase, free of impurities-single phase.

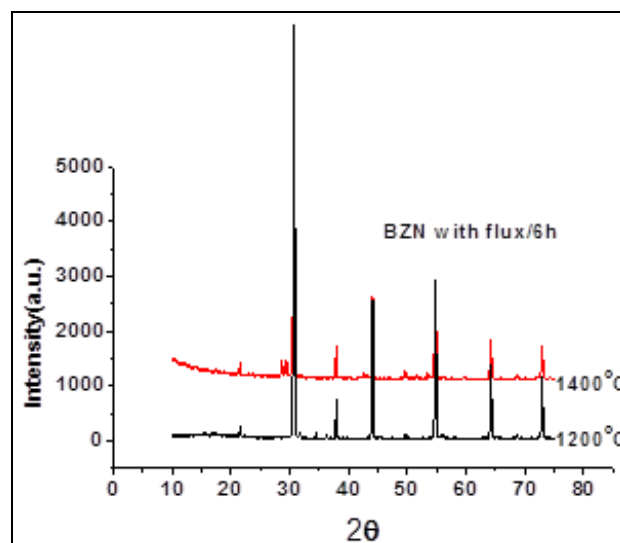


Fig 2: Powder XRD patterns of BZN with flux samples calcined at 1200 °C-1400 °C for 6hrs.

The fig.2 shows PXR patterns of the three samples with flux calcined for 6hrs at 1200-1400 °C. As evident from the plots the sample at 1200 °C crystallize in a pure perovskite single phase but at 1400 °C there appeared some new (impurity) peaks.

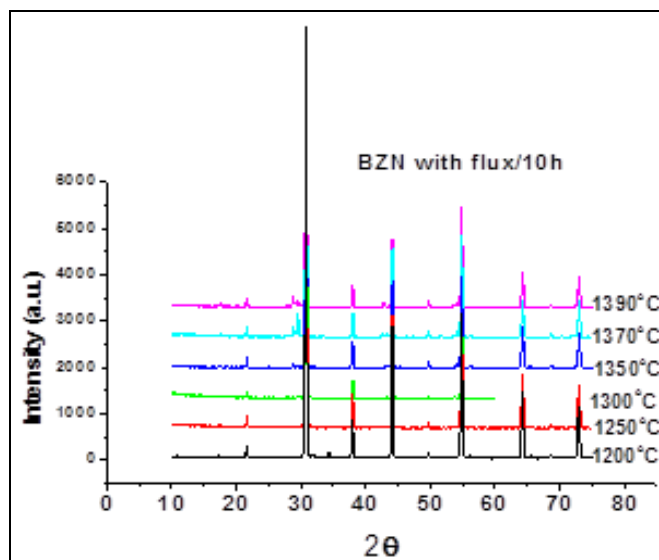


Fig 3: Powder XRD patterns of BZN with flux samples calcined at 1200 °C- 1390 °C for 10hrs.

The fig.3 shows powder XRD patterns of third set of six samples with flux which were calcined for 10 hrs at different temperatures: 1st sample at 1200 °C, 2nd sample at 1250 °C, 3rd sample at 1300 °C, 4th sample at 1350 °C, 5th sample at 1370 °C, and 6th sample at 1390 °C. As evident from the PXR patterns single phases were formed at the lower range

of temperatures 1200 °C to 1250 °C, however, beyond 1250 °C some new peaks (impurity) appeared.

The microstructures were observed using Field Emission Scanning Electron Microscopy (FESEM) on FEI quanta 3D FEG-FESEM coating the sample with Gold. Figures 4-6 show the SEM images of each of the samples.

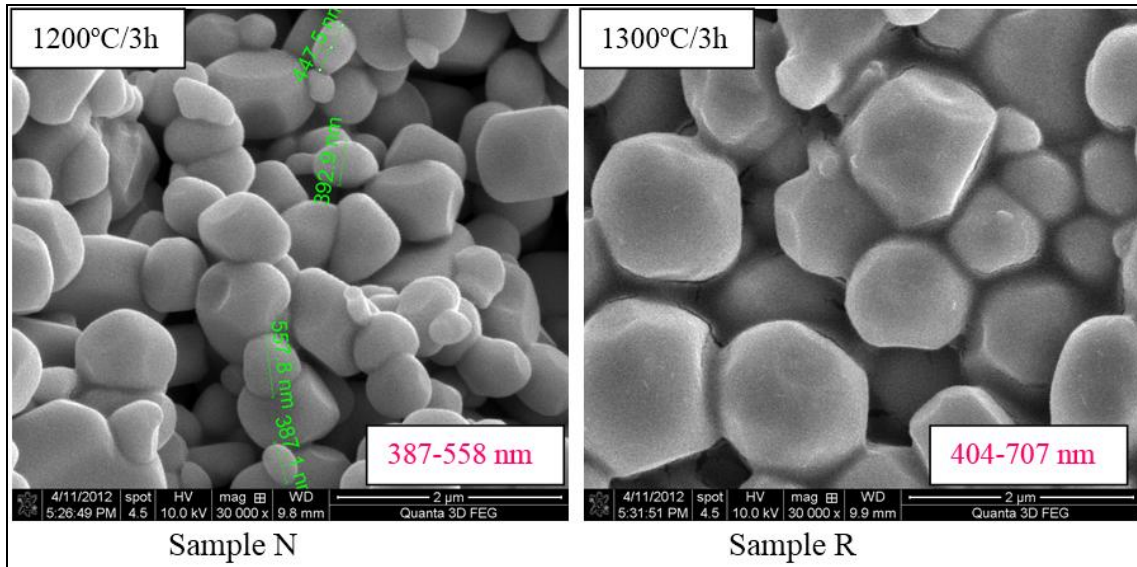


Fig 4: Scanning electron microscopy (SEM) images of BZN samples with flux calcined at temperatures 1200 °C and 1300 °C for 3hrs.

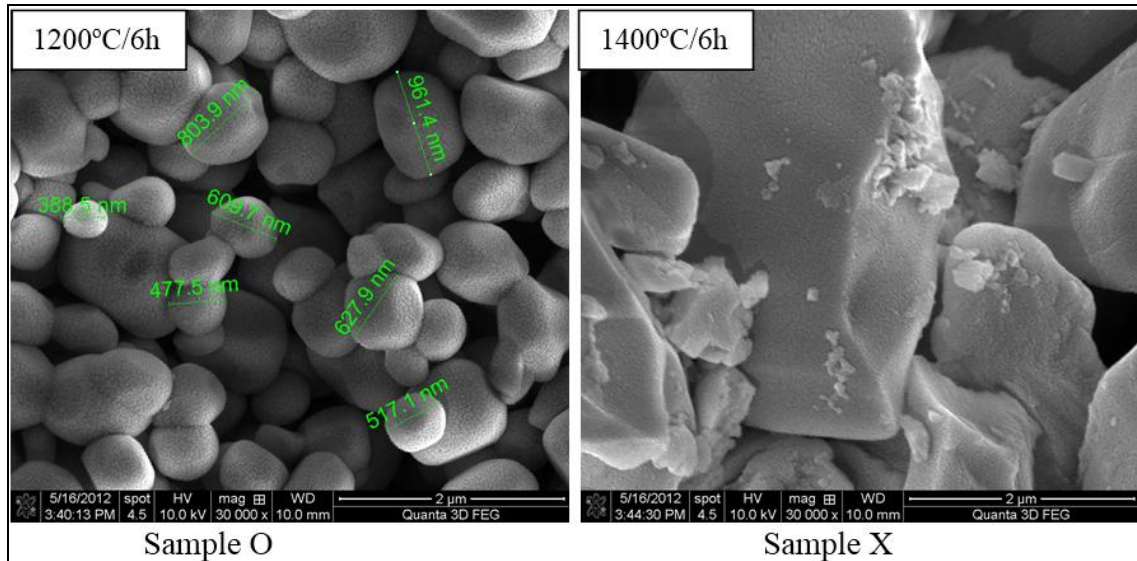


Fig 5: SEM images of BZN samples with flux calcined at temperatures 1200 °C and 1400 °C for 6hrs.

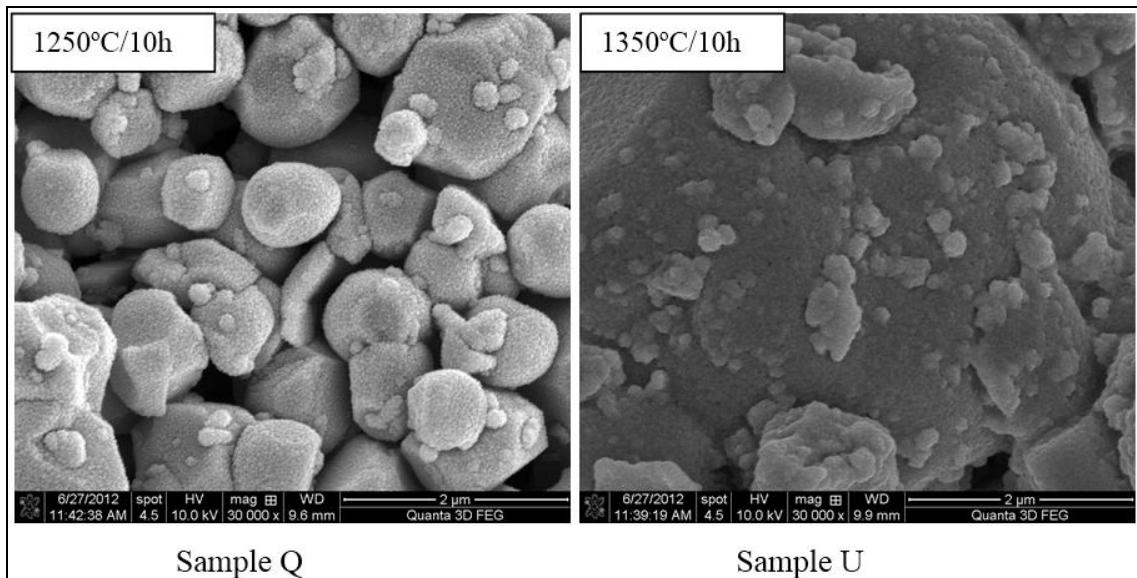


Fig 6: SEM images of BZN samples with flux calcined at temperatures 1250 °C- 1350 °C for 10hrs.

Result and discussion

XRD profiles of BZN powders with flux (Fig.1-3) calcined at various temperatures and durations show that the ceramics compositions are single phase, exclusively composed by BZN perovskite phase without crystallised secondary phase at temperatures 1200 °C-1300 °C of calcinations, however, for high calcinations (i.e. beyond 1300 °C) range of temperatures and durations formation of secondary phase has also been noticed. The secondary phase could be due to the formation of niobates Ba₄Nb₂O₉, Ba₅Nb₄O₁₅, and BaNb₂O₆. The formation of pure BZN perovskite phase at 1200°C demonstrates the fact that molten salt eutectic indeed accelerates the kinetics at this temperature by orders of magnitude and facilitates the formation of BZN. This could be attributed to the enhanced diffusion coefficients in the molten chloride liquid phase. 15

The samples calcined at 1200 °C/3h and 1300 °C/3h are more homogenised with spherical grains of average size 400-707nm. Both of them show higher packing. There is a drastic increase in packing, size of grains and homogeneity in their morphology.

Among the BZN samples with flux calcined at 1200 °C – 1390 °C for 10hrs the sample processed at 1200°C/10h only show pure, and homogeneous cuboidal shaped grains. The rest other (>1200 °C) shows conglomerate and formation of secondary phase.

Conclusions

Using this method Ba(Zn_{1/3}Nb_{2/3})O₃ (BZN) was successfully synthesized. The experimental data justify the fact that grain size depends on the initial time period of flux treatment. XRD results revealed that the flux (molten salts) acted as a mere solvent which accelerated the rate of formation of the desired BZN without interfering with the final compound. SEM analyses indicated that the calcinations temperature, time and flux played an important role in the development of BZN particle morphology. The formation of large grains with irregular shapes (at higher temperature range) could be a result of the variations on the kinetics of movement from boundary to boundary, since the grain-boundary energy is dependent on the grain-boundary orientation and grain-boundary mobility.16

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