

## Low temperature synthesis of barium Zinc niobate using flux

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### Abstract

Barium Zinc Niobate *i.e.*  $\text{Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (BZN) is a dielectric material and it has been employed in microwave communications. The single phase BZN powder was successfully prepared by using NaCl + KCl flux at the low temperature range 800-900°C. A systematic study indicating the effects of processing parameters, such as temperature, time, and amount of flux with respect to starting oxides, on the BZN formation mechanism and its resulting powder characteristics is reported. The phase compatibility, growth of particle size and difference in microstructures has been explained on the basis of powder XRD analyses and Scanning Electron Micrographs (SEM) images of the calcined samples.

**Keywords:** Microwave dielectric ceramics, Flux, XRD, SEM.

### Introduction

Microwave dielectric ceramics with high dielectric constant ( $\epsilon_r$ ), high quality factor ( $Q$ ), and small temperature coefficient ( $\tau_f$ ) are used as key materials of microwave devices in microwave communication systems, such as global communication satellites, cellular phones, radar detectors and police radar [1-3]. In the recent years, increasing demand of higher frequency ( $> 10\text{GHz}$ ) 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 BZT and BMT have been commercialized, in the last few years, economic factors associated with the high cost of  $\text{Ta}_2\text{O}_5$  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).<sup>7</sup> However, the resonance frequency temperature coefficient ( $\tau_f$ ) 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.<sup>9</sup> So, there is an increasing demand to discover alternate routes of synthesis by using flux (Molten Salt Synthesis-MSS) method [10,11].

It is the most cost-effective approach available for obtaining crystalline, chemically purified, single phase powders at lower temperatures, often in overall shorter reaction time with little residual impurities as compared with conventional solid-state reactions [12]. Grain size being the crucial factor for higher  $Q$  values [13] 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 [14]. 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 [15]. 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 [16].

The ceramics obtained by MSS method have larger grain size and higher B-site ordering parameter than that of the conventional mixed oxides ceramics at same sintering temperature [17]. The MSS technique has been used to synthesize several important complex perovskite materials by using NaCl-KCl eutectic salt mixture in which the eutectic temperature is 643 °C.

The processing of this material to yield an optimum performance is notoriously difficult as very small changes in bulk stoichiometry, cation ordering, and the degree of volatilization of ZnO at a high temperature can result in significant changes in the dielectric loss properties. Extensive deviations [18] from stoichiometry, for example through excessive volatilization of ZnO, cause the formation of secondary phases. Most investigations assigned the impurities to a variety of binary barium tantalates that include, but are not limited to,  $\text{Ba}_3\text{Ta}_2\text{O}_8$ ,  $\text{Ba}_5\text{Ta}_4\text{O}_{15}$ , and  $\text{BaTa}_2\text{O}_6$  (or niobates  $\text{Ba}_4\text{Nb}_2\text{O}_9$ ,  $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ , and  $\text{BaNb}_2\text{O}_6$ ); almost all of these secondary phases were believed to reduce  $Q$ . [19, 20].

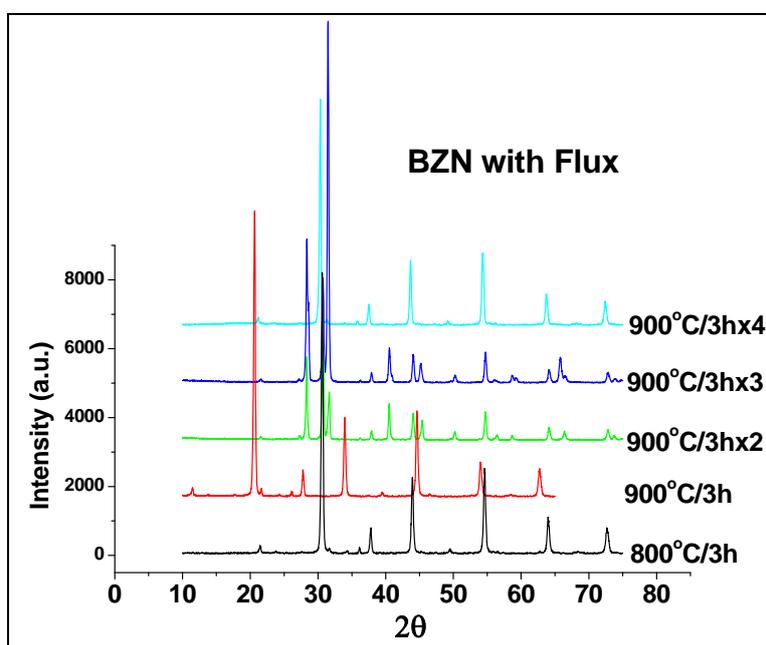
This paper explains how the processing conditions influence the properties and dielectric parameters of the materials. The aim of adopting different experimental conditions, varying in some cases temperature and other time, is to synthesize single phase which would be further used in ceramic pucks. The microwave dielectric properties were investigated in terms of the microstructural changes. 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. 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 powders were investigated.

**Experimental Procedure**

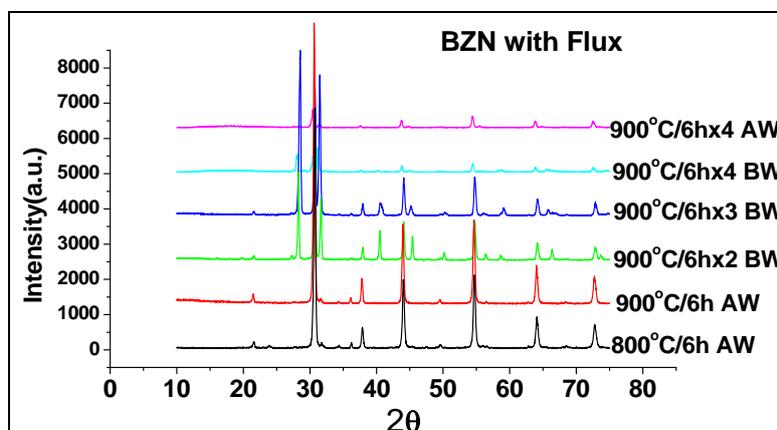
Different batches of samples of BZN composition with flux (Equimolar NaCl + KCl; Total weight of the salt to oxides 0.5) were prepared. The starting materials were BaCO<sub>3</sub> (99+ % Sigma Aldrich, USA), ZnO (99+ % Sigma Aldrich, USA), and Nb<sub>2</sub>O<sub>5</sub> (99.5% Alfa aesar, UK). The samples were ground in *acetone* for 1h using Agate mortar- pestle to obtain homogeneous mixtures and then calcined at 800 °C-900 °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<sub>3</sub>. The powders were then dried and subjected to characterizations. Powder XRD (Fig.1 & 2) of different samples undergone calcinations at various temperatures and durations were carried out and the samples were further examined (Fig.3) by using Field Emission Scanning Electron Microscopy (FESEM).

**Table1:** Samples compositions and processing summary

| Samples with flux | Calcinations    |
|-------------------|-----------------|
| A                 | 800 °C/6h       |
| B                 | 850 °C/3h       |
| C                 | 900 °C/3h       |
| D                 | 900 °C/3h       |
| E1                | 900 °C/(3hx2)   |
| E2                | 900 °C/(3hx3)   |
| E3                | 900 °C/(3hx4)   |
| F                 | 900 °C/6h       |
| G1                | 900 °C/6h       |
| G2                | 900 °C/(6h x 2) |
| G3                | 900 °C/(6h x 3) |
| G4                | 900 °C/(6h x 4) |



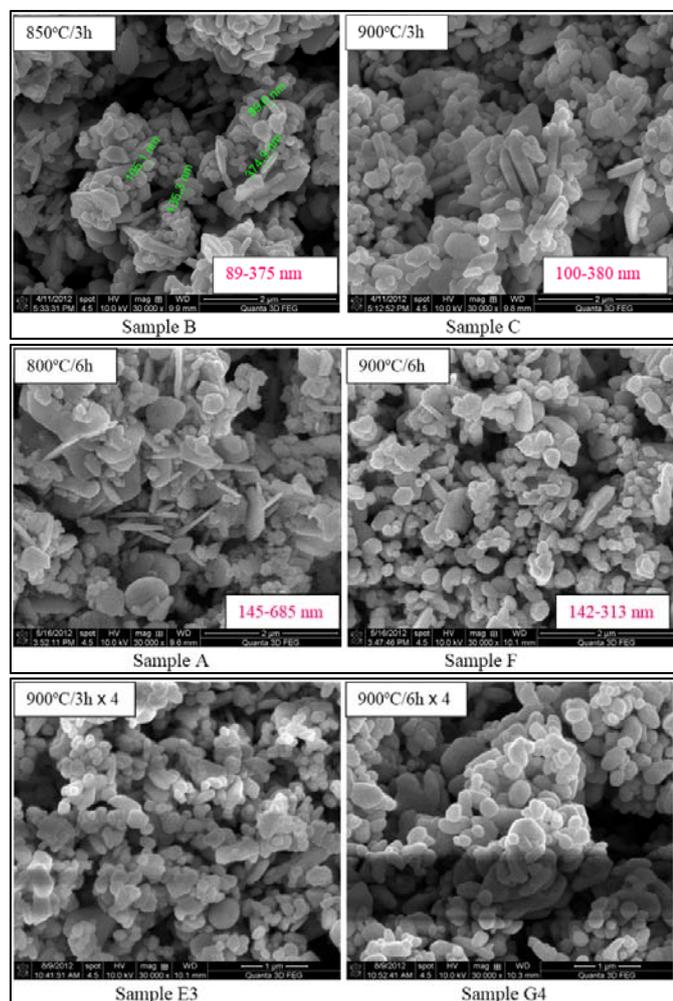
**Fig 1:** Powder XRD patterns of BZN with flux samples calcined at 800 °C- 900 °C for 3-12hrs. [All samples After Wash]



**Fig 2:** Powder XRD patterns of BZN with flux samples calcined at 800 °C- 900 °C for 6-24hrs. [AW= After Wash; BW= Before Wash]

The fig.1 shows PXRD patterns of five samples with flux which were calcined at 800-900 °C temperatures for three and multiples of three hours: 1<sup>st</sup> sample at 800 °C for 3hrs, 2<sup>nd</sup> sample at 900 °C for 3hrs, 3<sup>rd</sup> sample at 900 °C for 3hx2, 4<sup>th</sup> sample at 900 °C for 3hx3, and 5<sup>th</sup> sample at 900 °C for 3hx4. Similarly, fig.2 shows PXRD patterns of six samples with flux which were calcined at 800-900 °C but with different durations than before *i.e.* 6hrs and multiples of six hours: 1<sup>st</sup> sample at 800 °C for 6h, 2<sup>nd</sup> sample at 900 °C for 6h, 3<sup>rd</sup> sample at 900 °C for 6hx2, 4<sup>th</sup> sample at 900 °C for 6hx3, 5<sup>th</sup> and 6<sup>th</sup> samples at 900 °C for 6hx4; first, second and sixth samples after washing while the rest samples before washing the flux. It can be seen that all these samples crystallize in a pure perovskite phase, *i.e.* single phase- free of impurities.

The microstructures were observed using Field Emission Scanning Electron Microscopy (FESEM) on FEI quanta 3D FEG-FESEM coating the sample with Gold. Figures 3 below show the SEM images of some of the BZN samples *with flux* calcined at 800-900 °C for various durations.



**Fig 3:** Scanning electron microscopy (SEM) images of BZN samples with flux calcined at 800 °C- 900 °C for various durations.

### Result and discussion

The results of this study provide an explanation for the variations in particle size and crystal structure of BZN due to change in kinetics of its synthesis. Powder XRD profiles of BZN powders with flux calcined at various temperatures and

durations (Fig.1 & 2) show that the ceramics compositions are single phase, exclusively composed by BZN perovskite phase without crystallised secondary phase at lower temperatures (800 °C-900 °C) of calcinations. The formation of pure BZN perovskite phase even at a temperature of 800 °C demonstrates the fact that molten salt eutectic indeed accelerates the kinetics at this low 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 [21-24]. Figure 3 shows SEM microstructure of the calcined BZN samples at different experimental conditions. The micrograph indicates the average particle size of the calcined powders in the range of 89–960 nm. The samples calcined at 850 °C/3h and that at 900 °C/3h have submicron crystallites with average size of 89-373nm and 100-380nm respectively. The grains are not uniform, some are quadrate while some are rod or cylindrical in shapes. The sample calcined at 900 °C/3h is comparatively more packed. The sample calcined at 800 °C/6h show some needle shaped as well as some spherical grains with much variation in average grain size 145-685 nm. There is very significant increment in the grain size and packing both in comparison to that of 850 °C/3h calcined sample. The sample calcined at 900 °C/6h show improved homogeneity with quadrate shape grains. These revealed that the 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 of flux treatment.

### Conclusions

Ba(Zn<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub> was successfully synthesized at a low temperature (800-900 °C) and short time (3-6 hrs) of heating using NaCl-KCl flux *i.e.* molten salt synthesis (MSS). The experimental data justify the fact that grain size depends on the initial time period of flux treatment.

XRD results revealed that the 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.

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