EFFECT OF STRONTIUM OXIDE ON GRAIN GROWTH AND DENSIFICATION IN BNN SYSTEM

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Abstract

Grain size and density parameters have been investigated in SrO added Tungsten Bronze (TB) type Ferroelectric Barium Sodium Niobate (BNN) ceramic as a function of sintering time and sintering temperature. Addition of SrO has greatly improved the density of the system. The sample BNN with 3% SrO has showed above 95% of theoretical density. Scanning Electron Micrographs revealed normal grain growth in the present study. Activation energies for the formation of grain growth and densification in all the samples have been estimated and found lying in the range of 50-60 kcal/mole. The results are discussed in the light of present understanding.

Keywords: Strontium Oxide, Grain Growth, Densification, Activation Energy.

Introduction

Ceramic Barium Sodium Niobate (BNN) has been emphasized by many workers as the most promising candidate material for electro-optic and non-linear optic applications [1, 2, 3, 4]. Attempts have been made to prepare dense niobate by the addition of certain dopants such as Li_2O and MnO_2 [5].The primary difficulty encountered in the sintering of BNN appears to be the volatilization of sodium oxide at high temperatures. Shen-LiFu et al.[6] and Ravez et al. [7] achieved better sintering of PLZT and TB type systems respectively with the aid of doping of dopants [8,9] such as Li-Bi, Na-Bi, Na-B and fluorine.

The present study of sintering behavior and grain growth of BNN with the addition of SrO was taken up with the aim of improving upon its sinterability.

Experimental

The material was prepared employing usual ceramic fabrication techniques. Reagent grade $BaCO_3$, Na_2CO_3, Nb_2O_5 and $SrCO_3$ in appropriate amounts were wet mixed using agate mortar and pestle and the resulting mixture was dried in an oven. The powder was pre-fired overnight at 950^0C in air atmosphere. The pre-fired powder was dry milled again for few hours to get a particle size of approximately 1 μ m. The powder was then sieved and granulated by means of PVA (Poly Vinyl Alcohol) as binder and pressed at 8000 psi in the form of discs (10 mm dia and 2mm thickness).

The discs so obtained were fired at temperatures ranging from 1150-1250^0C in air for different times. Density measurements were done by water immersion technique (ASTM-71) and for microstructure observations polished discs were used.

Results

X-Ray diffraction Analysis. The X-ray diffractograms of pure and SrO doped samples of BNN were obtained. Pure BNN Sample exhibited single phase having a tetragonal TB structure with a = 12.451Å, c= 3.998 Å which compares favorably with the published data [10]. The SrO doped samples also showed a tetragonal TB structure with a slightly different lattice constants.

Densification and Activation Energy for densification. The influence of SrO on the densification behavior of BNN presented in Fig.1, which is a plot of sintered density (A,B,C,D) and porosity ($A^{'}$, $B^{'}$, $C^{'}$, $D^{'}$) as a function of sintering time at various sintering temperatures.

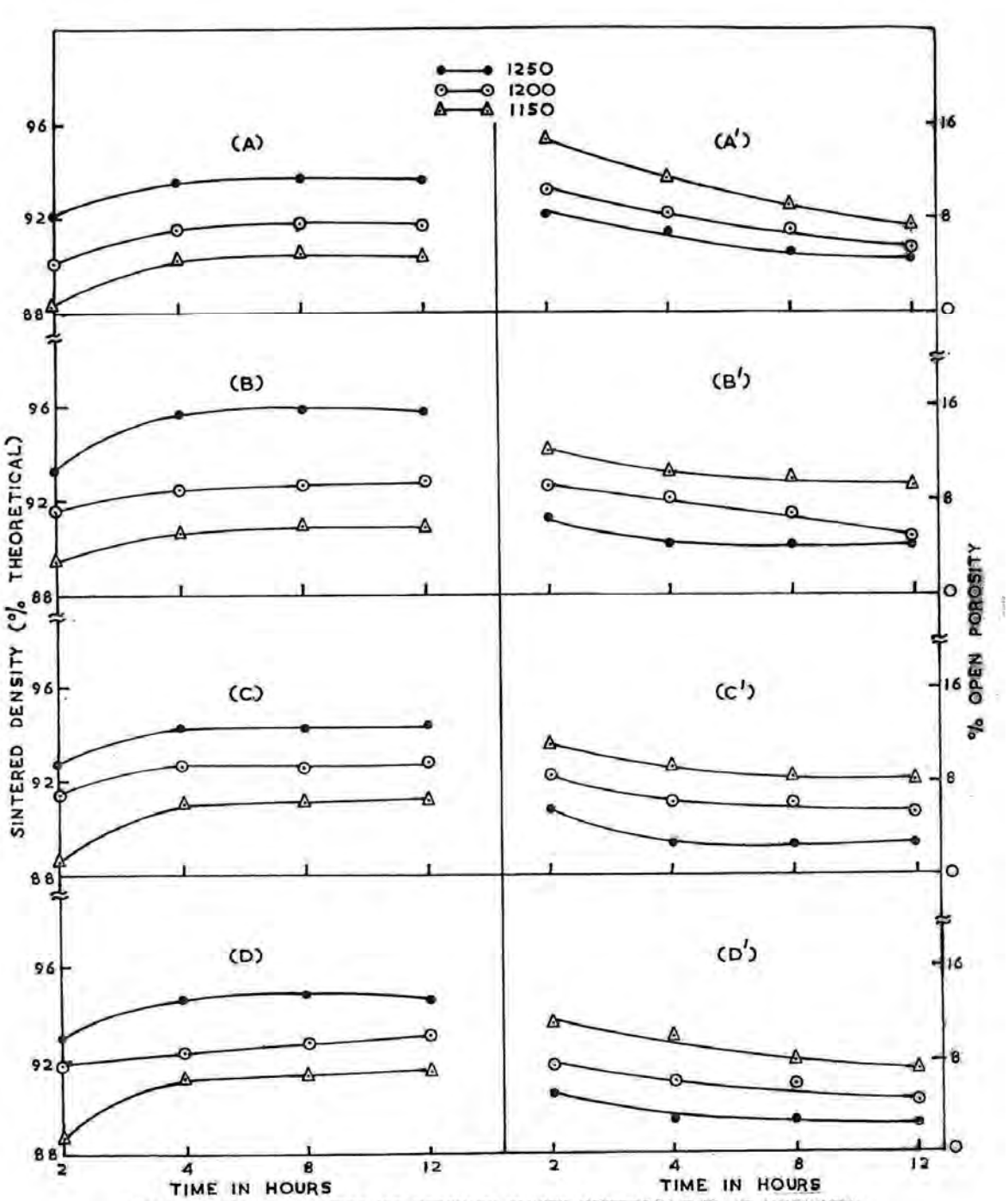

FIG.1. SINTERED DENSITY AND POROSITY VERSUS SINTERING TIME AT DIFFERENT SINTERING TEMPERATURES FOR THE SYSTEM (A) BNN (B) BNN + 1 wt% SrO (C) BNN + 2 wt% SrO (D) BNN + 3 wt% SrO

The Activation energy for densification is calculated from the Arrhenius rate equation (Fig.2).

$$\frac{1}{t} = K_0 \exp\left(-\frac{Q_D}{RT}\right) \tag{1}$$

where t is the sintering time required for the desired densification, Q_D is the activation energy for densification, K_0 is the constant. The activation energies for the densification are listed in table 1.

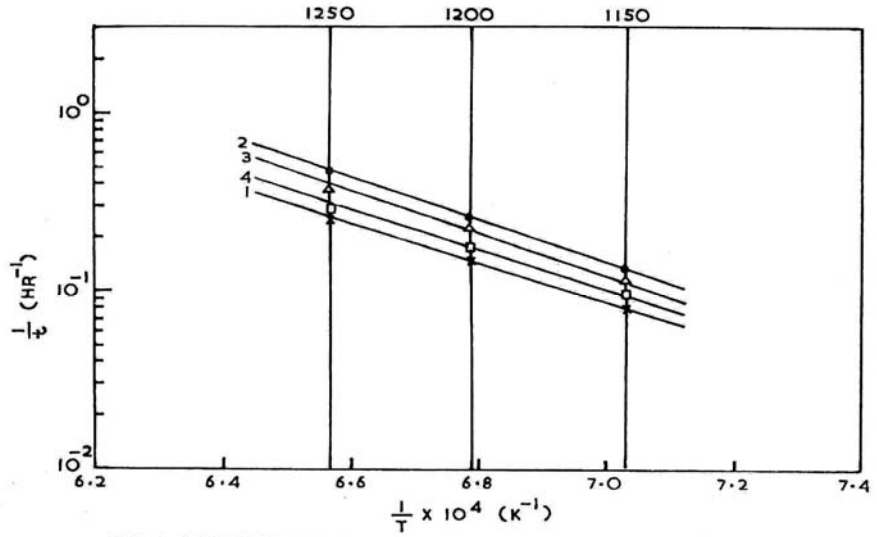

FIG.2 ARRHENIUS PLOT OF DENSIFICATION RATE CONSTANT (1/t) AS A FUNCTION OF INVERSE SINTERING TEMPERATURE (1/T) FOR THE SYSTEM (1) BNN (2) BNN + 1 wt% SrO (3) BNN + 2 wt% SrO (4) BNN + 3 wt% SrO

Table 1. Activation energies for the densification

Composition	Activation Energy [kcal/mole]
BNN	50.4
BNN+1wt% SrO	51.6
BNN+2wt% SrO	54.6
BNN+3 wt% SrO	57.2

Grain Growth. Normal pore free grain growth is obtained for 2wt% SrO BNN compositions. Figs.3, 4, 5 shows a plot of grain size versus sintering time at various sintering temperature. Typical scanning electron micrographs of the doped and undoped BNN compositions are shown in Fig. 6. The variation of inverse of square of grain diameter with sintering time resulted in a straight line and as such the grain growth follows a rate equation $D^2 - D_O^2 = Kt$, where D_0 the initial particle is size and K is the rate constant. The activation energy for grain growth is estimated following the rate equation

$$K = K_O \exp\left(-\frac{Q_G}{RT}\right) \tag{2}$$

where Q_G is the activation energy for grain growth.

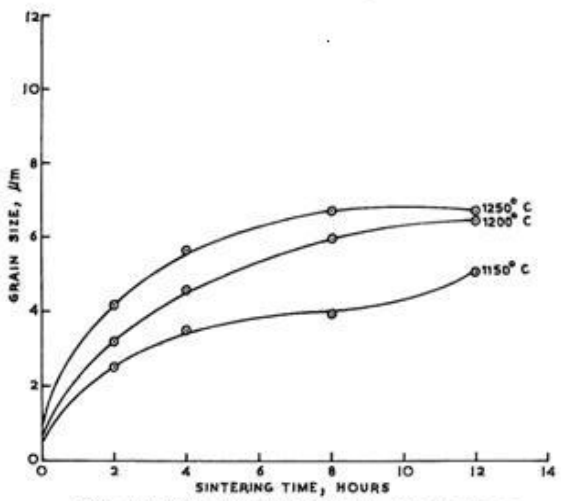

FIG.3. VARIATION OF GRAIN SIZE WITH SINTERING TIME FOR THE SYSTEM BNN + 1 wt% SrO

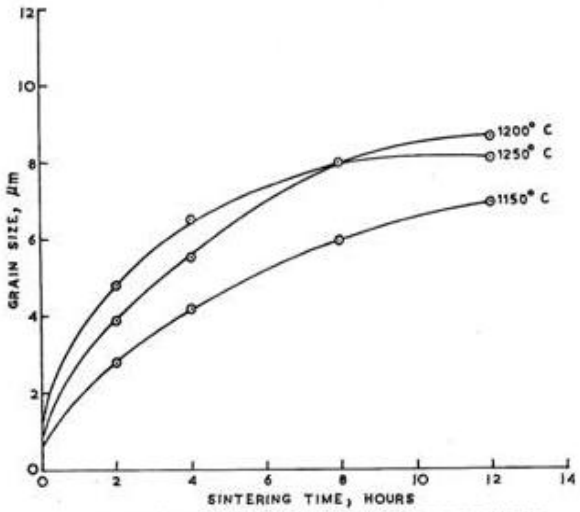

FIG.4. VARIATION OF GRAIN SIZE WITH SINTRING TIME FOR THE SYSTEM BNN + 2 wt% SrO

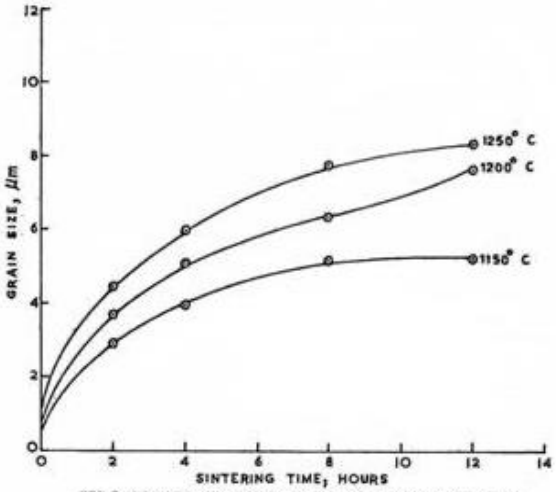

FIG.5. VARIATION OF GRAIN SIZE WITH SINTERING TIME FOR THE SYSTEM BNN + 3 wt% SrO

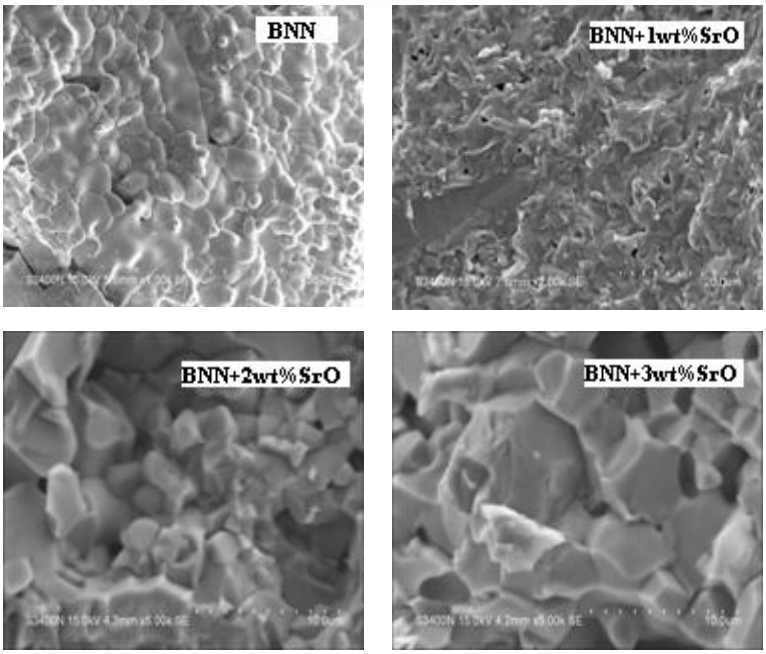

FIG.6. TYPICAL SEM IMAGES OF DOPED AND UNDOPED BNN CERAMICS

Activation energies for the grain growth are listed in table 2.

Table 2. Activation energies for grain growth

Composition	Activation Energy [kcal/mole]
BNN	49.8
BNN+1wt% SrO	50.5
BNN+2wt% SrO	53.4
BNN+3 wt% SrO	56.2

Discussion

The rate of grain growth is decided by the rate at which a curved grain boundary approaches its centre of curvature, which is controlled by the bulk diffusivity of the slowest moving ion in ceramics. The densification rate is on the other hand controlled by the rate of pore removal. Various mechanisms like bulk diffusion, surface diffusion and evaporation –condensation, ect. have been proposed for pore removal during sintering. The same values of activation energies for densification and grain growth in the present case indicates that the same mechanism, i.e., the bulk diffusion of the slowest moving ion, controles the rate of densification and grain growth [11, 12, 13, 14].

Conclusions

3 wt% SrO addition improves the sintering of BNN and densities more than 95% of the theoretical value are achieved.

Acknowledgments

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