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# Synthesis, DC conductivity and Dielectric studies on double doped Strontium Bismuth Niobate Ceramics

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## Abstract

The Strontium Bismuth Niobate  $\text{SrBi}_2\text{Nb}_2\text{O}_9$  (SBN),  $\text{K}_{0.025}\text{Sr}_{0.95}\text{Gd}_{0.025}\text{Bi}_2\text{Nb}_2\text{O}_9$  (KSGBN1) and  $\text{K}_{0.05}\text{Sr}_{0.9}\text{Gd}_{0.05}\text{Bi}_2\text{Nb}_2\text{O}_9$  (KSGBN2) ceramics were prepared by two stage solid state reaction method. Crystal structure of sintered samples was studied by powder X - ray diffraction technique. XRD patterns well matched with reported data (ICSD #82280). The lattice parameters of the samples were calculated using POWD Software. Pellets of 10mm diameter and thickness about 1mm~2mm were prepared and final sintered in the temperature range 900°C ~950°C for four hours. The surface morphology of the samples was studied from Scanning electron Microscope pictures. The Temperature dependence of DC conductivity and dielectric properties were obtained and analyzed. Conclusions arrived at are presented.

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*Keywords:* DC conductivity; Dielectric; Ferroelectrics; SEM and XRD

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## 1. Introduction

There is lot of demand in the electronic manufacturing industry for ferroelectric material electronic devices, such as nonvolatile ferroelectric random access memories (NVFRAM), capacitors, resonators, piezoelectric sensors, pyroelectric infrared detectors and optical switches [1-3], due to their unique physical properties. Non-volatility, high read-write speed, low operating power and radiation hardness makes NVFRAMs a promising candidate in the arena of semiconductor memories [4-7].

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Aurivillius compounds are described by the general formula  $\text{Bi}_2\text{A}_{m-1}\text{B}_m\text{O}_{3m+3}$  ( $m=1, 2, 3, 4$ ), where A is a combination of ions suitable for dodecahedral coordination and B is a combination of ions suitable for octahedral coordination [5-7]. These compounds consists of two structural elements, namely  $[\text{Bi}_2\text{O}_2]^{2+}$  layers and perovskite-type structures having the composition  $(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$ . Strontium Bismuth Niobate (SBN) and Strontium Bismuth Tantalate (SBT) belong to Bismuth Layer Structured Ferroelectrics (BLSF) with general formula  $\text{ABi}_2\text{B}_2\text{O}_9$  ( $m=2$ ) [6], where A site can accommodate mono, di and trivalent ions and B site can accommodate ions like  $\text{Nb}^{+5}$ ,  $\text{Ta}^{+5}$  and  $\text{Ti}^{+4}$ . The advantage of BLSFs over other ferroelectric materials is due to the fact that they have intermediate bismuth oxide layers  $(\text{Bi}_2\text{O}_2)^{2+}$  between the ferroelectric units  $(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$ . BLSFs have high Curie temperature ( $T_c$ ), low dielectric loss and high anisotropy in the layered structure [8]. The fatigue-free behaviour of (SBT) was reported by Araujo *et al* [8] has gained importance among Lead-free ferroelectric materials for electronic memory applications.

Literature evidences that the properties of pure SBT, Bismuth Strontium Niobate (SBN) can be further improved by partial substitution of ‘A’ and ‘B’ sites with elements like Lanthanum, Yttrium, Barium etc. [9-14]. In the present work an attempt is being made to further enhance the properties of SBN as NVFRAM material by partial substitution at the ‘A’ site (Strontium) with the elements Potassium and Gadolinium. These elements are selected for doping in view of their ionic radii and electronegativity values. The ionic radii [15] of the elements K, Sr and Gd are 1.64 Å, 1.18 Å, 1.11 Å and electro negativity values are 0.8 eV, 1.0eV, 1.2eV respectively. Ionic radius of K is larger than Sr, while that of Gd is lesser. Electronegativity of K is lesser than Sr, while that of Gd is more.

## 2. Experimental

The samples SBN, KSGBN1 and KSGBN2 were prepared by two stage solid state reaction method. Mixtures of  $\text{K}_2\text{CO}_3$ ,  $\text{SrCO}_3$ ,  $\text{Gd}_2\text{O}_3$ ,  $\text{Bi}_2\text{O}_3$  and  $\text{Nb}_2\text{O}_5$  of Sigma-Aldrich (purity > 99.9%) were used as the starting materials in stoichiometric proportion. 3% excess  $\text{Bi}_2\text{O}_3$  was taken to compensate loss due to evaporation. They are thoroughly ground in agate-mortar for about 6 hours and then primarily sintered at  $850^\circ\text{C} \sim 900^\circ\text{C}$  for 4 hours. Calcined powder is admixed with Poly Vinyl Alcohol (PVA) binder and pressed into pellets of 10 mm diameter and 1mm ~ 2 mm thickness by uniaxial pressing in hydraulic jack. While preparing pellets the applied pressure was about 10 MPa. These pellets were then final sintered for 4 h at  $900^\circ\text{C} \sim 950^\circ\text{C}$ . The phase formation of the samples was verified by X-ray powder diffraction (XRD) analysis (Using PANalytical X’pert diffractometer, model number PW 3040/60). Lattice parameters and Miller indices of the samples were calculated using POWD software. Structure of the grains was studied from scanning electron microscopy (SEM) (Carl ZEISS EVO18) images. Electrodes were formed by applying silver paste on both sides of the polished pellets. The temperature dependence of the dielectric constant ‘ $\epsilon$ ’ was measured at different frequencies on HP 4192A impedance analyzer in the temperature range from RT to  $500^\circ\text{C}$ . DC conductivity of the samples was measured using Keithley 617 electrometer.

## 3. Results and Discussion

### 3.1 Structural Properties

The XRD patterns of the samples: Standard SBN (ICSD # 82280)[16], Experimental SBN, KSGBN1 and KSGBN2 are shown in figure1. XRD peaks of prepared samples are matching with the peaks of standard SBN and no extra peaks were observed. It indicates that the elements potassium (K) and Gadolinium (Gd) diffused well into SBN lattice and a new single phase solid solution of Aurivillius family of ceramics has been formed. The  $2\theta$  value of the intense peak (h k l : 1 1 5) slightly decreased on increasing the percentage of doping. It indicates a decrease in inter-planar spacing for (1 1 5) plane. This may be attributed to comparatively smaller ionic radius of Gd to that of the space available at A (Sr) site. Peak broadening is also observed indicating structural disturbance in the crystal due to strain. Lattice parameters a, b, c and unit cell volume V of the samples obtained from POWD software are shown in Table 1. Theoretical density of the samples is calculated and compared with the experimental values. As the doping concentration increased, the porosity decreased.

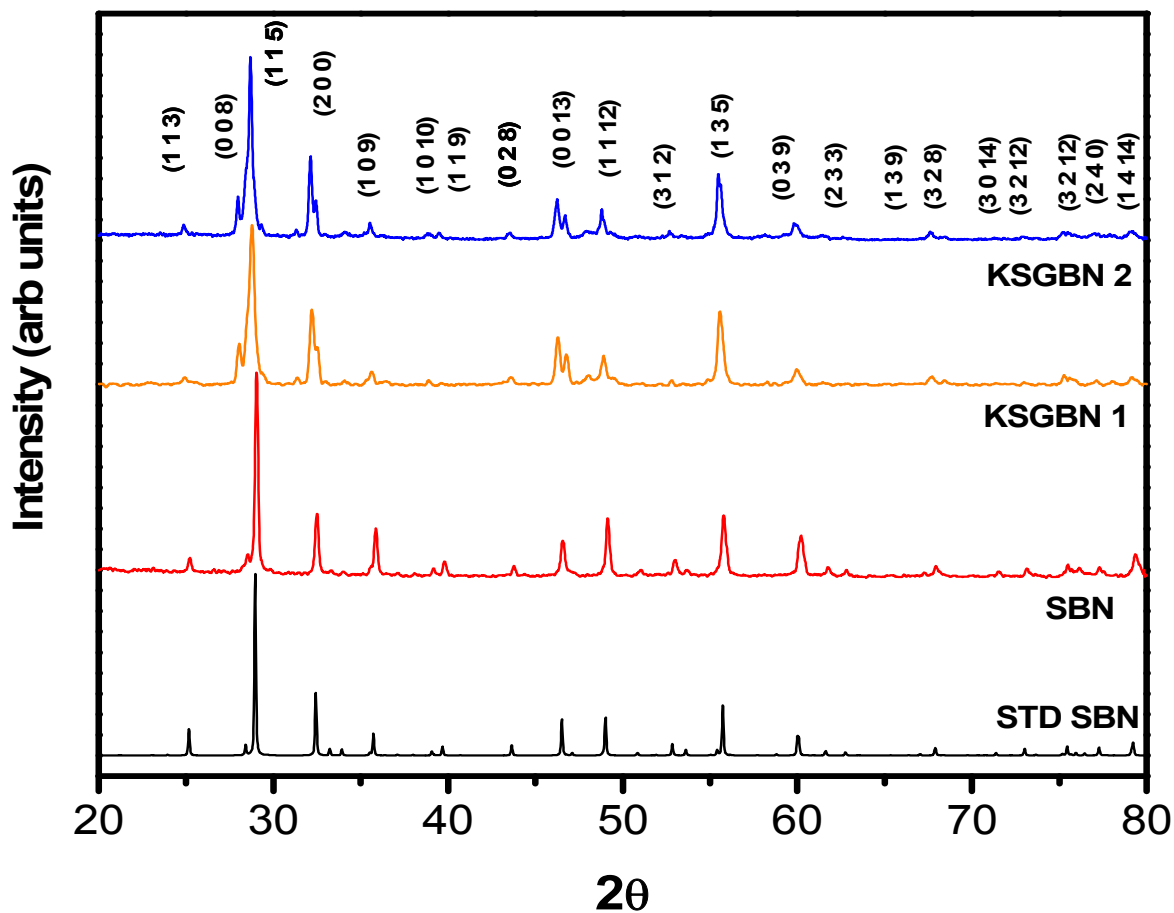


Fig. 1: XRD patterns of Standard SBN (ICSD #82280), SBN Experimental(SBN), KSGBN1 and KSGBN2

TABLE 1: Comparison of lattice parameters, unit cell volume, theoretical and experimental densities of the samples SBN, KSGBN1 and KSGBN2

| Sample Name | Lattice parameters |                   |                   | b/a   | Unit Cell Volume V in $\text{\AA}^3$ | Density in $\text{gm/cm}^3$ |              | Activation Energy ( $E_a$ ) in eV |
|-------------|--------------------|-------------------|-------------------|-------|--------------------------------------|-----------------------------|--------------|-----------------------------------|
|             | a in $\text{\AA}$  | b in $\text{\AA}$ | c in $\text{\AA}$ |       |                                      | Theoretical                 | Experimental |                                   |
| SBN STD     | 5.518              | 5.515             | 25.112            | 0.999 | 764.39                               | 7.260                       | ---          | ---                               |
| SBN         | 5.523              | 5.508             | 25.032            | 0.997 | 761.64                               | 7.295                       | 6.998        | 1.083                             |
| KSGBN1      | 5.546              | 5.513             | 25.139            | 0.994 | 768.85                               | 7.219                       | 6.235        | 0.8523                            |
| KSGBN2      | 5.549              | 5.507             | 25.019            | 0.992 | 764.63                               | 7.264                       | 6.501        | 0.8934                            |

SEM pictures shown in figure 2 also conform the presence of porosity in the samples. Randomly oriented grains are observed in the samples. On increasing the doping concentration, the grain size decreased

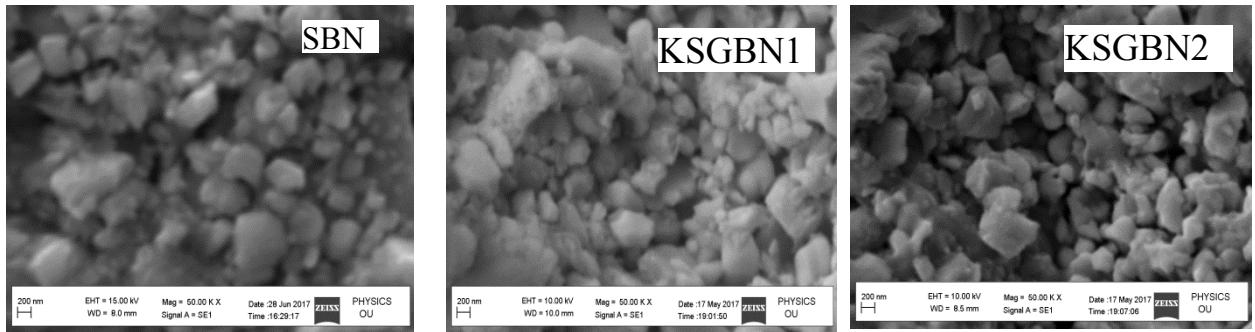


Fig.2: SEM images of SBN, KSGBN1 and KSGBN2

### 3.2 Electrical Properties

#### (i) Dielectric properties:

Temperature dependence of dielectric constant  $\epsilon$  measured at 1 kHz, 5 kHz and 10 kHz frequencies from room temperature (RT) to 450°C temperature are shown in figure 3. For all the samples the  $\epsilon$  value is about 150 at RT. Ferroelectric materials are characterized by a transition temperature called Curie temperature ( $T_c$ ) at which the  $\epsilon$  is maximum. At this temperature lattice structure changes from orthorhombic to tetragonal. For the present samples  $T_c$  changed from 445°C for SBN to 449°C for KSGBN1 and then to 444°C for KSGBN2. Small variation in  $T_c$  observed may be due to the phenomenon of strain produced by one dopant being compensated by strain produced in opposite direction by the other. At  $T_c$  the material changes from ferroelectric phase to paraelectric phase [9]. All the samples studied showed more or less normal ferroelectric behavior and as it appears from fig (3), do not deviate much from Curie-Weiss law.

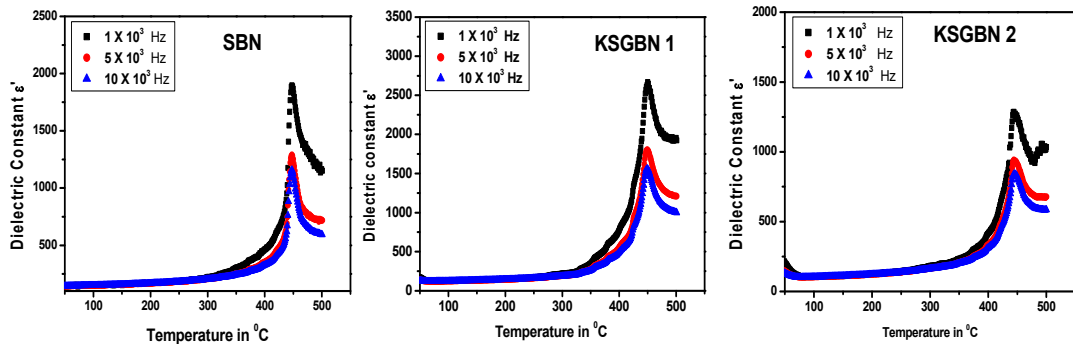


Fig3: Variation of Dielectric constant with temperature of SBN, KSGBN1 and KSGBN2

#### (ii) DC conductivity:

Figure 4 shows the variation of  $\log_{10}(\sigma)$  as a function of inverse of absolute temperature of the prepared samples. From dielectric studies the  $T_c$  is found around 440°C ~450°C where the materials change from ferroelectric to paraelectric phase. Hence, the range of temperatures were chosen from 200°C ~350°C, which are sufficiently below the  $T_c$ . It is evident that the conduction is increasing with the temperature and follows NTCR behavior. The DC conductivity in dielectric materials is mainly due to the anion motion [17]. The oxygen vacancies present in the ceramic samples and the “charge carriers – vacancy” pairs generated by thermal agitation contribute for the conduction by hopping mechanism [18].

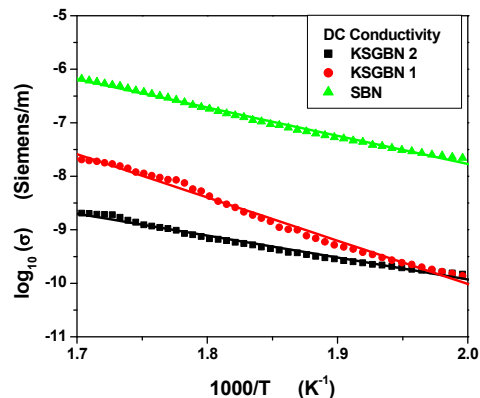


Fig4: Variation of  $\ln_{10}\sigma$  with  $1000/TK$  of SBN, KSGBN1 and KSGBN2

Temperature ( $1000/T$  K) Vs  $\ln \sigma$  curves are almost linear over the range of temperatures of interest. Activation energy ( $E_a$ ) for the prepared samples is given in table 1. When compared with the un-doped sample SBN, it decreased in KSGBN1 and KSGBN2. Meanwhile, it is slightly more in KSGBN2 than of KSGBN1. Experimental density of the samples also changed in the same manner.

#### 4. Conclusions

A new set of BLSF-O<sub>9</sub> compounds have been formed with double doping at A site. XRD obtained confirmed presence of orthorhombic structure similar to the parent compound. SEM shows cube like well-formed uniform grains. XRD showed very small shift in  $2\theta$  values, which indicate a feeble structural distortion. However this lattice distortion did not affect the  $T_C$  value of the newly formed compounds. The increase in DC conductivity may be attributed to the decrease in density. The conduction due to DC applied field is contributed by anions only. No other conduction mechanism is found. In depth studies are required to completely understand the ferroelectric nature of these samples.

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