ABSTRACT

Recent environmental concerns, stresses the need to develop lead-free ferroelectric materials. Barium Strontium Titanate (BST) with the general formula $Ba_{1-x}Sr_xTiO_3$, has a perovskite structure and Strontium Barium Niobate (SBN) with the general formula $Sr_xBa_{1-x}Nb_2O_6$, has a Tetragonal Tungsten Bronze (TTB) structure are considered as promising lead-free ferroelectric materials. Unlike most of the ferroelectric materials that exhibit ferroelectric phase only for a particular composition, the BST and SBN materials exhibit ferroelectricity over wide composition range between $0.01 \leq x \leq 0.30$ and $0.20 \leq x \leq 0.80$, with the high dielectric constant with tunable Curie temperature (T_c). In the present work, BST and SBN has been synthesized by solid state method, with different compositions to achieve high dielectric constant with tunable T_c for ferroelectric application. This is first time ever, a successful attempt has been made to obtain Abnormal Grain Growth (AGG) and duplex microstructure free BST and SBN materials in the selected compositional range.

Strontium Nitrate [$Sr(NO_3)_2$], Barium Nitrate [$Ba(NO_3)_2$] and Titanium dioxide [TiO_2] were the precursors used to prepare BST with composition ranging from $0.01 \leq x \leq 0.3$ (BST05,BST10,BST15,BST20, BST25 and BST30),The BST samples were calcined at 1200 ^{O}C based DSC and TG studies. The samples were then pelletized and microwave sintered. Initially the sintering temperature was fixed at 1250 ^{O}C, But SEM analysis indicated incomplete or coalesced grains formation based on which the sintering temperature was raised to 1400 ^{O}C. The X-Ray diffraction (XRD) patterns of all the sintered BST compositions confirmed the complete perovskite phase formation at 1400 ^{O}C. The transmission electron microscopy (TEM) images of the BST powder exhibits sharp edges with no degree of agglomeration and particles size was around 400 nm. All samples, except

BST25 and BST30, exhibit similar morphology with uniform grain distribution with pronounced layered/faceted grain microstructure and no coalesced grains. Also, the uniform grain distribution represents a well-packed microstructure, free from AGG, duplex microstructure and pores. The average grain size ranged between 3 to 10 µm for all BST compositions. In dielectric studies, a broader and diffused peak confirmed the finely grained BST ceramics. When the Strontium (Sr) concentration increases, the dielectric constant increased and the Curie temperature shifts towards lower temperature. Ferroelectric hysteresis (F-E) loop measurements of all BST compositions were studied at the frequency of 10 Hz. The loops were broad for all BST compositions. However, increase in Sr content decreases the broadness of loops. All the BST compositions, except BST25 and BST30 exhibit piezoelectric nature.

In SBN, the precursors where $Sr(NO_3)_2$, $Ba(NO_3)_2$ and Niobium pentoxide [Nb_2O_5] were used and various compositions of $Sr_xBa_{1-x}Nb_2O_6$ [x= 0.40(SBN40), 0.45(SBN45), 0.50(SBN50), 0.55(SBN55), and 0.60 (SBN60)] were synthesized by solid-state reaction method. The X-ray diffraction pattern of the calcined (1200 ^{O}C based on DSC and TG studies) SBN indicates the Tetragonal Tungsten Bronze (TTB) phase of SBN. However, additional peaks were observed for $x \geq 0.5$ which indicates the formation of strontium niobate (SN) phase, predominant at x = 0.50, 0.55 and 0.60. It reveals that the calcination temperature was not sufficient to complete the TTB phase formation for higher Sr concentration. Further, the lattice parameters varied with increase in Sr content which was evident from XRD studies. The samples were then pelletized and microwave sintered at 1350 ^{O}C. The XRD pattern of sintered SBN at 1350 ^{O}C confirmed the completed formation of TTB crystalline phase without any presence of secondary phases such as SN and Barium Niobate (BN). Further, no significant variation in lattice constants was observed. The Transmission Electron Microscopy (TEM) was employed to determine the particle size and morphology of the prepared SBN compositions. The average particle size was observed around (~400 nm) and the particle shows sharp edges with no degree of agglomeration. The ring patterns in selected area electron diffraction (SAED) pattern of all SBN compositions reveals the polycrystalline nature. The high-resolution TEM image of SBN confirmed that the d-spacing value was closely related to planes of atoms in the crystalline lattice. The microstructure of the SBN compositions exhibits uniform grain distribution of particles. Also, it reveals a well-packed rod-like microstructure, free from Abnormal Grain Growth (AGG), duplex microstructure and pores. The grain size of SBN was increased with increase in Sr/Barium (Ba) ratio. The temperature dependence real part permittivity for all the SBN compositions shows a diffused phase transition of SBN and exhibits a typical relaxor ferroelectric behavior. The broad diffused phase transition observed in SBN45, SBN50 and SBN55 compositions was due to the non-uniform distribution of grain size. The room temperature ferroelectric hysteresis (F-E) loop measurement reveals the broad loops for all SBN compositions which confirm the ferroelectric nature. At a particular electric field, the value of polarization was found to decrease with increase in Sr concentration in all the SBN compositions. These results can be explained by considering the growth in grain size with increase in Sr content. Moreover, The piezoelectric coefficient (d_{33}) values of SBN were calculated.

In conclusion, the linear and tunable behavior of T_c in the BST and SBN compositions reduce the complexity in fabricating tunable microwave devices, phase shifters, etc.