Dielectric Relaxation Behaviour of $(Bi_{0.2}Na_{0.2}Ba_{0.2}Sr_{0.2}Ca_{0.2})TiO_3$ High-Entropy Ceramic

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Abstract

High entropy materials are a relatively young new class of materials discovered in 2003. It possesses four kinds of special core effects as a result of its strong mixing nature such as (i) High entropy effect, (ii) Severe lattice distortion effect, (iii) Sluggish diffusion effect, and (iv) Cocktail effect. High Entropy Ceramics (HECs) are defined as the solid solutions of inorganic compounds (five or more cations sublattices) with one or more Wykoff sites shared by equal or nearly equal atomic ratios of multi-principal elements. HECs have gained the attention of researchers due to their fascinating properties. In this report, an A-site disordered high entropy perovskite $(Bi_{0.2}Na_{0.2}Ba_{0.2}Sr_{0.2}Ca_{0.2})TiO_3$ ceramic was prepared via a solid-state reaction route. The XRD pattern and FESEM-EDS confirmed the formation of a single-phase solid solution with a tetragonal structure. A detailed study of the dielectric behaviour of the sample was done. Modified Curie-Weiss law was fitted to the relative permittivity to analyze the relaxor behaviour of the sample. HECs are highly tolerant to ions and their properties can be tailored by composition and according to the application purposes.

Introduction

Recently High Entropy concept has opened the path toward the material composition design. The configurational entropy of a system can be depicted as [1]

$$S_{\text{config}} = -R\left[\left(\sum_{a=1}^{A} x_a \ln x_a + \sum_{b=1}^{B} x_b \ln x_b\right)_{\text{cation-site}} + \left(\sum_{j=1}^{M} x_j \ln x_j\right)_{\text{anion-site}}\right] \quad (1)$$

where A, B, and M represent the elements present in A-site, B-site, and no of elements in both cationic and anionic sites, x_a, x_b, and x_j are the mole fraction of corresponding elements and R is the gas constant.

According to the previous literature, the ionic size difference (δ) is a key element for regulating the formation of a single-phase compound. The A-site cation ionic size difference can be defined as [2]

$$\delta(R_A) = \sqrt{\sum_{i=1}^{N} c_i\left[1 - r_{A_i}/\left(\sum_{i=1}^{N} c_i\, r_{A_i}\right)\right]^2} \quad (2)$$

where, r_{A_i} is the ionic radius of A-site elements of ith component, c_i is the molar fraction.

Also, the Goldschmidt tolerance factor (t) is an essential parameter for the stability of a perovskite structure.

The tolerance factor [3] can be given as -

$$t = \frac{(R_A + R_O)}{\sqrt{2}(R_B + R_O)} \quad (3)$$

where R_A, R_B, and R_O are the ionic radii of A, B, and Oxygen sites in perovskite oxides.

For the cubic phase, t ~1, t>1 for tetragonal/hexagonal and t<1 for the orthorhombic/octahedral phase. In this report, the structural and dielectric relaxation of an A-site modified $(Bi_{0.2}Na_{0.2}Ba_{0.2}Sr_{0.2}Ca_{0.2})TiO_3$ (BNBSCT), synthesized via solid state reaction route assisted with ball milling are discussed. The atomic size difference and tolerance factor are calculated as 6.37% and 1.003. The values suggest the formation of a single-phase A-site disordered compound [4].

Method

Figure 1: Schematic representation of the synthesis and characterization of BNBSCT

Discussion

Figure 2 shows the room temperature XRD pattern of the studied sample. The pattern depicts a typical and pure single-phase perovskite structure. The sharp and intense peak indicates the high crystalline nature of the sample. The splitting of (200) reflex around 45° illustrates the tetragonal crystal structure of the sample. Also, the pattern is matched by X'Pert HighScore Plus software to standard reference data (ICDD-98-005-7923), which also reveals the above. The surface morphology and chemical composition of the synthesized sample are investigated by using a Field Emission Scanning Electron Microscope (FESEM) in addition to Energy Dispersive X-ray Spectroscopy (EDS). The inset of Figure 2 shows the FESEM and EDS spectra. Figure 3 shows the pie chart of atomic % and weight % of the constituent elements analysed from EDS.
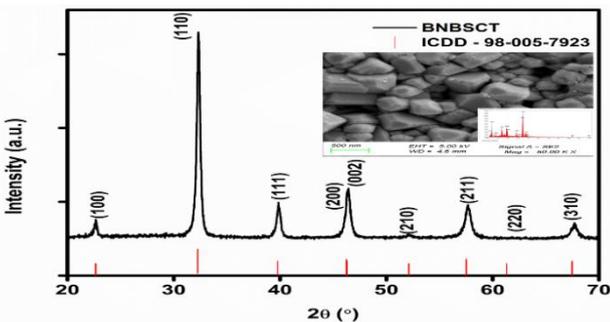

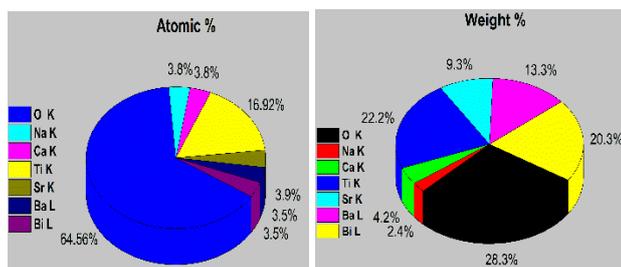**Figure 2:** Room temperature XRD pattern and FESEM micrograph of the studied sample

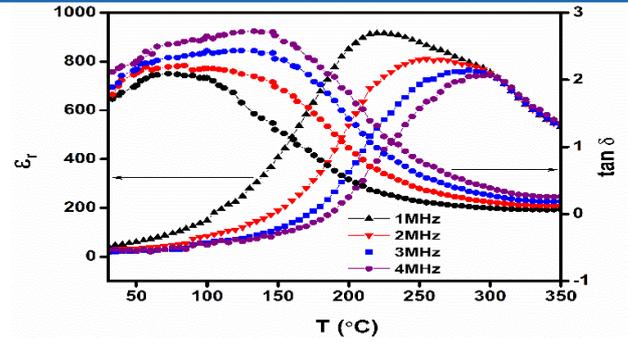**Figure 3:** FESEM micrograph, weight%, and atomic % of BNBSCT

Figure 4: Variation of dielectric constant and loss with temperature at various frequencies and

The dielectric properties of the sample are shown in Figure 4. The Figure shows the variation of dielectric parameters with temperature (25-350 °C) at different frequencies (1-4MHz). The graph shows an obvious dispersion below T$_m$ (Temperature corresponding to maximum dielectric constant). This is attributed to the strain factor and disordered structure, which leads to the destruction of long-range ordered ferroelectric domains that ignite the formation of polar nano-micro regions (PNRs) [5]. Hence the variation in the speed of the dielectric response of PNRs with different sizes leads to dielectric relaxation. The strong frequency dispersion behaviour depicts the ferroelectric relaxor. The dielectric loss also showed a frequency dispersion behaviour. The loss is higher at a high frequency than at a lower frequency. Furthermore, the loss tangent values are suppressed significantly at above T$_m$.

To investigate the relaxation behaviour of the studied sample, the Modified Curie-Weiss (MCW) law is fitted to the dielectric permittivity [6]

$$\frac{1}{\varepsilon_r} - \frac{1}{\varepsilon_m} = \frac{(T-T_m)^\gamma}{C}, T > T_m$$

where ε$_m$ refers to the maximum of ε$_r$ and C is the constant. The parameter γ known as the diffusivity constant, which indicates the degree of diffusion. Generally, it ranges from 1 (for normal ferroelectric) to 2 (for ideal relaxation ferroelectric). The γ value is calculated from the slope of the graph as shown in Figure 5 The value ranges from 1.24-1.98, which suggests the BNBSCT is a relaxor ferroelectric. The relaxation behaviour in HECs possibly arises from chemical disorders and distorted structure.
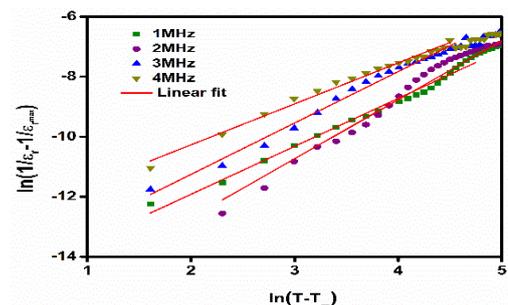

Figure 5: MCW fitting to the dielectric permittivity

Conclusion and Future Prospective

To summarize, we have synthesized an A-site disordered single-phase HEC. The XRD and FESEM-EDS pattern reveals the tetragonal crystal structure, perfect microstructure, and purity of the sample. The diffused phase transition and shifting of T$_m$ signify the relaxor behaviour of BNBSCT. Also, the value of the diffusivity constant found from the MCW fitting to the dielectric constant agrees with the relaxor behaviour of the studied sample. As the sample shows relaxor behaviour, it may show a high energy storage efficiency.

Acknowledgment

References

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