

Preparation and Characterization of $\text{Ba}(\text{Fe}_{1/4}\text{Ti}_{1/2}\text{V}_{1/4})\text{O}_3$ with BaTiO_3

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Abstract

$\text{Ba}(\text{Fe}_{1/4}\text{Ti}_{1/2}\text{V}_{1/4})\text{O}_3$ perovskite was synthesized by solid state reaction method. XRD, microstructure and dielectric properties were analyzed in this study. The compound has hexagonal perovskite structure having grain size of 0.44 μm . The dielectric constant (ϵ_r) and loss tangent ($\tan\delta$) of the samples were determined at different temperatures (32 °C-500 °C) in the frequency range 100 Hz –1 MHz. The microwave dielectric measurements were also carried out in the X-band frequency range (9 GHz -12 GHz) at room temperature. Maximum ϵ_r was observed at low frequencies and it decreases monotonically with the increase of frequency. ϵ_r and $\tan \delta$ increases with increasing temperature. At microwave frequency, also we find the similar behaviour of ϵ_r . The value of ϵ_r is 11.5 at 9 GHz.

Keywords: $\text{Ba}(\text{Fe}_{1/4}\text{Ti}_{1/2}\text{V}_{1/4})\text{O}_3$, Microwave ceramics synthesis, Structure, Microstructure, Dielectric measurements, X-band frequency range

Introduction

The complex compound $\text{Ba}(\text{Fe}_{1/4}\text{Ti}_{1/2}\text{V}_{1/4})\text{O}_3$ is a member of perovskite structural family of general formula ABO_3 (A=mono or divalent, B=tri, tetra, penta or hexavalent ions). It is interesting to note that the substitution of B-site cations with aliovalent dopant yield a number of complex compounds shows typical ceramic properties [1-4] Many researchers have done a lot of work on modified barium titanate and niobates having general formula $\text{Ba}(\text{B}'_{1/3}\text{B}''_{2/3})\text{O}_3$ [5-8]

To our knowledge, it has been found that no systematic work has been done on the complex compounds $\text{Ba}(\text{Fe}_{1/4}\text{Ti}_{1/2}\text{V}_{1/4})\text{O}_3$. Therefore, we have carried out

investigations on structural and dielectric properties of the compound. In this paper, we report the preparation, preliminary structural and dielectric properties of BFTV ceramic sample.

Experimental

A solid state reaction technique was used to prepare BFTV which is shown in Figure 1. Powder X-ray diffraction (XRD) was obtained by crushing the sintered specimen for phase identification and calculation of lattice parameters using X-ray diffractometer (Philips PRO, PANalytical) data was collected using Cu-K α radiation in the 2θ range of 20° to 70° with a scanning rate of $2^\circ/\text{minute}$ at room temperature. The surface morphology and grain size were obtained from SEM micrographs. Dielectric characterizations were performed on sintered pellets coated with silver paint on both the sides of the sample by using LCR meter (HIOKI, 312C model).

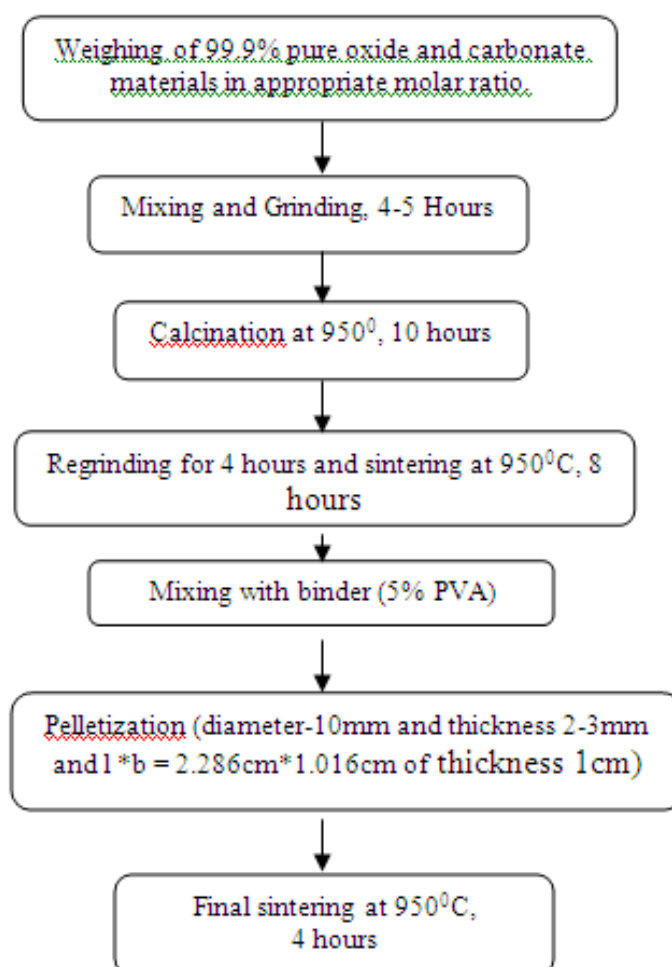


Figure 1: Procedure for the Synthesis of Sample by Solid State Reaction Technique

The dielectric properties of the sintered samples were measured at low frequencies (100 Hz-1MHz) as well as at X-band frequency (9 GHz-12 GHz). The microwave bench set up [4] for the measurement of dielectric constant is shown in Fig 2.

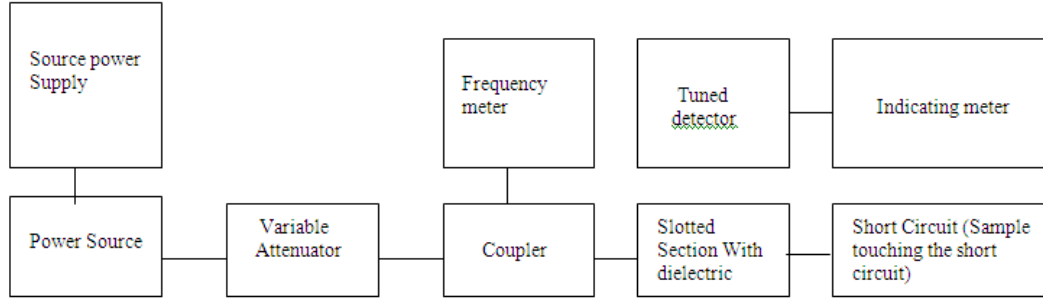


Figure 2: Setup for Measuring Dielectric Constant

Different microwave dielectric parameters were estimated from the following standard formula:

$$\epsilon = \frac{(a/\pi)^2 \left(\frac{X}{l_\epsilon} \right)^2 + 1}{\left(\frac{2a}{\lambda_g} \right)^2 + 1} \quad (1)$$

Where $a = 2.286$ cms, l_ϵ = thickness of sample, λ_g = Guided wavelength, $X = \tan x/x$, $\tan x/x = \tan \beta(l_\epsilon + D_R - D) / \beta l_\epsilon$, $\beta = 2\pi/\lambda_g$, D_R = position of minimum without Sample and D = position of minimum with sample

Results and Discussion

Fig.3 shows x-ray diffraction pattern of BFTV sample. The unit cell volume, x-ray density and particle size were calculated and listed in Table 1. From the x-ray analysis, the structure of the synthesized compound is found to have hexagonal crystal symmetry. Experimentally observed (d_{obs}) and calculated d-spacing with their intensities for all the compounds were compared. Min-Han Kim [5] reported that $Ba(Zn_{1/3}Ta_{2/3})O_3$ (BZT) perovskite changes its structure from 1:2 ordered hexagonal to cubic structure by the addition of SnO_2 and ZrO_2 . Because the ionic radius of Sn^{4+} and Zn^{2+} ion is approximately equal. But TiO_2 added BZT retains the hexagonal structure as it is. Since the ionic radius of the Ti^{4+} ion is much smaller than that of Zn^{2+} ion. In case of our prepared sample also, it retains hexagonal structure because Ti^{4+} ion is much smaller than Fe^{2+} and V^{5+} .

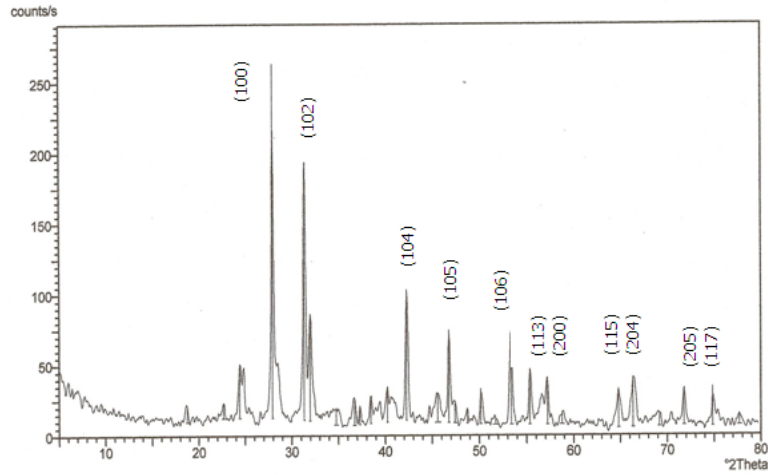


Figure 3: X-Ray Diffraction Pattern of BFTV

Table 1: Crystallographic Data of BFTV

Unit cell parameters	a	3.716 Å
	c	11.389 Å
Unit cell volume	V	136.22 (Å) ³
X-ray density	ρ	25.89 gm/cm ³
Particle size	p	32.24 nm

Figure 4 displays SEM micrograph of BFTV shows bimodal grains having irregular shapes with the average grain size of 0.44 μm . Our sample has grain size $<1 \mu\text{m}$ because the sintering temperature was 950⁰ C and Si-Yoon Noh [6] reported that the average grain size of the specimen increases with increasing sintering temperature.

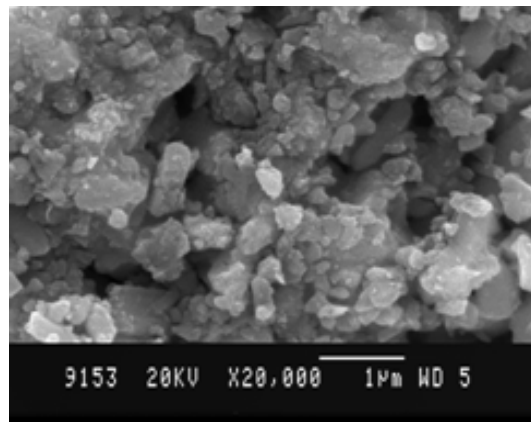


Figure 4: SEM Micrograph of BFTV

The variation of dielectric constant ϵ_r and loss tangent ($\tan\delta$) of BFTV with frequency at different temperatures shown in Figure 5. a) and b) shows a strong dependence of ϵ_r is observed in the frequency range 100 Hz–10 KHz and then remains constant almost upto 1 MHz. Dispersion in ϵ_r shows presence of interfacial polarization. Since the material has been prepared by the ceramic technique, there is a possibility of micro heterogeneities which give rise to piling up of mobile charge carriers at the grain boundary, producing interfacial polarization giving rise to high value of ϵ_r .

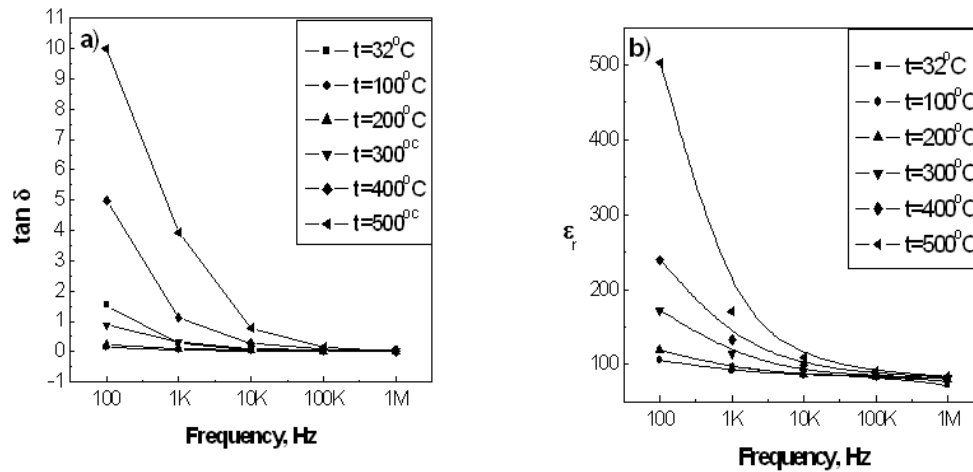


Figure 5: a) Variation of $\tan\delta$ with Frequency at Various Temperatures b) Variation of ϵ_r with Frequency at Various Temperatures

At higher frequencies, (>10 KHz) due to faster periodic reversal of the field, the perturbation of thermal motion of ionic or molecular dipole takes place, which produces a net dipolar orientation in the direction of applied field and hence dipolar polarization becomes more prominent at these frequencies. This is the reason for the initial decrease and later steadiness in the value of ϵ_r and $\tan\delta$ of these ceramics [7].

It is also observed that the dispersion in ϵ_r becomes more pronounced with increase in temperature. This may be related to the fact that, at high temperatures, the loss is dominated by the thermally activated electron hopping where as at lower temperature; such an activated process is frozen out, resulting in a lesser variation of ϵ_r at low temperature [8].

The dielectric characteristics measured in the microwave frequency range i.e. 9-12 GHz, shown in Figure 7 (i) depicts the decrease in dielectric constant ϵ_r with the increase in the frequency, which is normal behaviour of ferroelectrics. From Fig. 7(iii), it is observed that as frequency increases the loss also increases. Figure 7 (ii) shows that, Qxf value first increases and reaches peak then decreases. We got very low value of Q . Qxf value decreases for the aliovalent substituted systems [9]. The isovalent substitution will improve the Qxf values. Ching - Liang Hung et al., reported that if the difference between positive and negative ionic radius became

larger, there is increase in damping factor [10]. The increase of the damping factor caused larger microwave loss. This is the reason for getting higher loss at microwave frequencies.

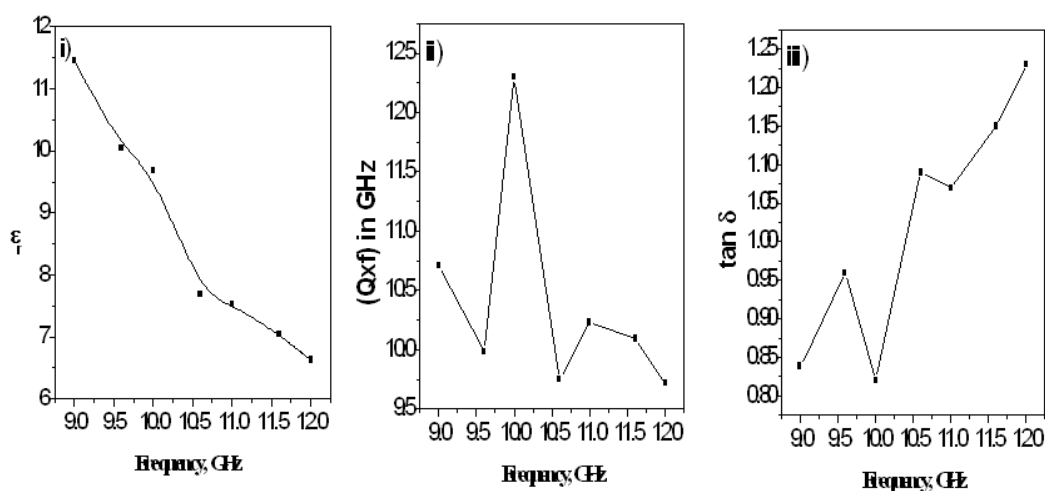


Figure 7: Frequency dependence of (i) dielectric constant ϵ_r , (ii) (Qxf), and (iii) Dielectric loss for BFTV

Conclusion

The modified BFTV ceramic prepared by solid state reaction method showed the hexagonal crystal symmetry. From SEM the particle size is calculated and is found to be 0.44 μm . The sample has $\epsilon_r = 95.55$ at 1 kHz and $\epsilon_r = 72.42$ at 1 MHz. The same ceramic has ϵ_r of 11.46 at 9 GHz. At microwave frequency, the sample may be exhibited very low value of ϵ_r and high $\tan \delta$ due to low sintering temperature. This low permittivity dielectrics ($\epsilon_r < 15$) may be used for insulation when used as a substrate for components where their dielectric properties are of greater importance.

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