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VARIATION IN DIELECTRIC PROPERTIES OF COMPOSITE CERAMICS: LITHIUM FERRITE SUBSTITUTED BARIUM TITANATE

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Abstract: Ferroelectric-Ferrite composite with composition (x) $Li_{0.5}Fe_{2.5}O_4$ + (1-x) $BaTiO_3$ (for x= 0, 0.20 & 0.40) were prepared by the conventional sintering technique at 900°C for 4 hours. Presence of two phases is further confirmed by x-ray diffraction analysis and lowering of c/a ratio show incorporation of ferrite in ferroelectric compound. Dielectric constant decreases with increase in ferrite content indicating lowering contribution due to interfacial polarization. An increase of Curie temperature with increase in ferrite content suggests an increase of material stability in high temperature region.

Key words: *Titanates, Sintering, X-ray diffraction, Dielectric properties.*

Introduction

$BaTiO_3$, is one of the important ferroelectric material with high dielectric constant, low Curie temperature[1] and substitution with any ion in

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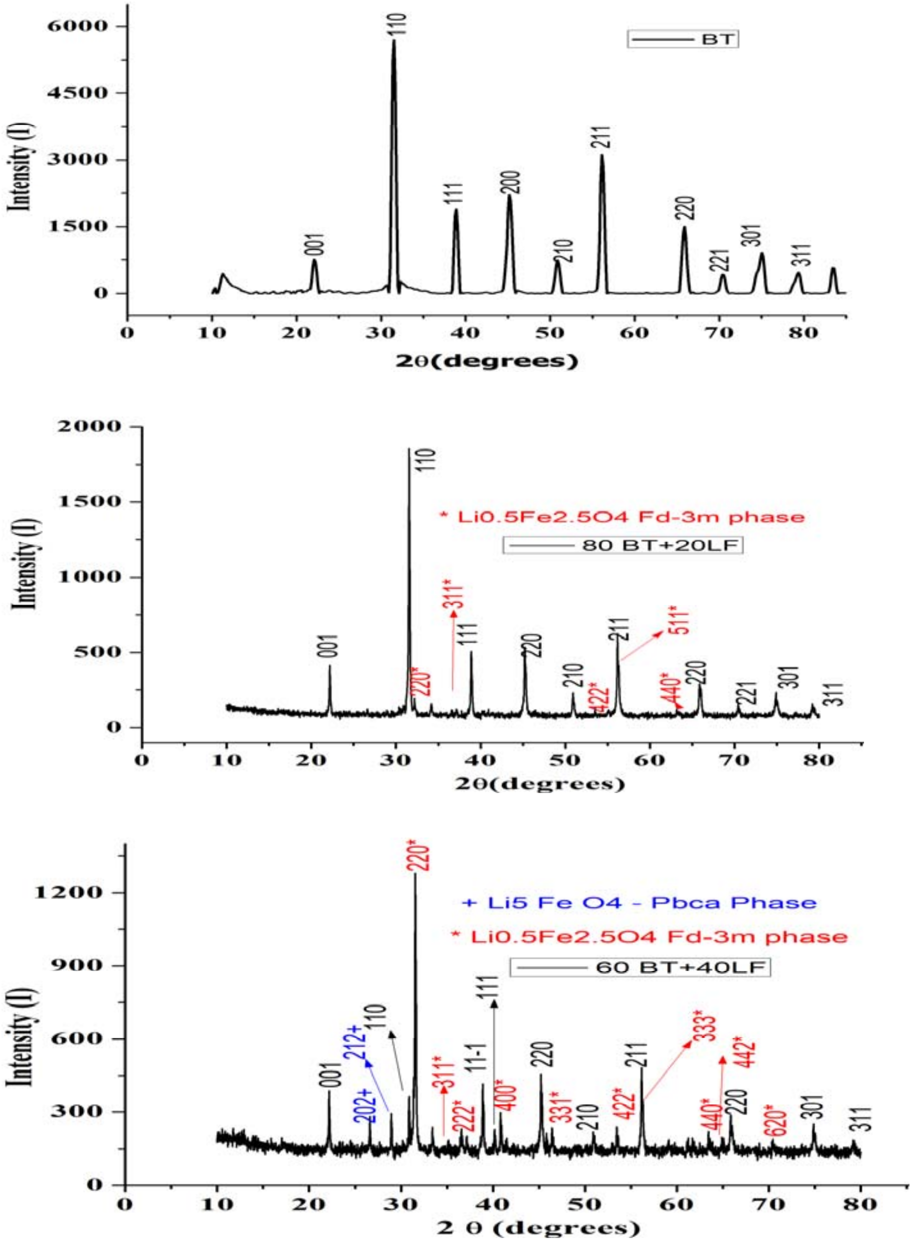
$BaTiO_3$ structure upgrades any of property.[2-3] Substituting ferrite in barium titanate showed enhanced magnetic property.[4] Enhancement of magnetic property in ferrite/$BaTiO_3$ structure is attributed to presence of ferrite grains, leading to accumulation of magnetism. Composite materials possess both ferroelectric and magnetic phases simultaneously due to combine effect among the constituent phases. Presence of ferrite grains also improves the dielectric nature of the composite by which stability is attained when used for higher frequency applications.[5] In composites, the mutual interaction between ferroelectric and ferromagnetic phases results in high magnetoelectric coupling effect results in high magnetoelectric response.[6-7] With increase in lithium ferrite content, saturation magnetization has converse nature with respect to saturation polarization.[8] As per our previous investigations, doping of lithium ferrite in $BaTiO_3$ with low concentration, improved the dielectric nature.[8] With further increase in lithium ferrite, it may be expected to achieve higher Curie temperature with good ferroelectric properties in the material, especially at high frequency range (1-3GHz).

Experimental

Polycrystalline lithium ferrite substituted barium titanate ceramics were prepared using conventional solid-state sintering technique. Lithium carbonate (Li_2CO_3) and iron oxide (Fe_2O_3), powders of AR grade were thoroughly mixed and calcinated in powder form at 800°C for 4 hours to get lithium ferrite (LF). Barium carbonate ($BaCo_3$) and titanium oxide (TiO_2) powders were grinded, sintered at 900°C for 4 hours to obtain barium titanate (BT). Powders of lithium ferrite and barium titanate were mixed in weight percentages (for $x= 0, 0.20, 0.40$) and grinded. Composites powers were pressed at high pressure into pellets and pre sintered at 1000°C for 4 hours. X-ray analysis showed the presence of both $BaTiO_3$ and lithium ferrite phases. Samples were grinded again and sintered at 1150°C for 4 hours to obtain (x) $Li_{0.5}Fe_{2.5}O_4$+ (1-x) $BaTiO_3$ (for x= 0.20 & 0.40). The formation of phase of lithium ferrite was identified using x-ray diffraction (Model: Bruker D8 SSS-Cu Kα). Fourier transform infrared spectroscopy (FTIR) was measured using with Bruker, Germany Model: Vertex 70. Permittivity measurement was carried out using impedance analyzer (Model: Agilent technologies model E5062A) for higher frequency range up to 3 GHz under room temperature conditions. Dielectric constant versus temperature measurement a low frequency (10 kHz) was carried to understand the polarization mechanism under temperature condition for lithium ferrite.

Results and discussions

Figure 1 shows the XRD patterns for the investigated samples showing no traces of additional impurities and peaks identified, indexed as per constituent phase for both ferroelectric-ferrite. Single tetragonal phase corresponding to P4mm has been identified for $BaTiO_3$ material, and in case of 80% $BaTiO_3$ and 20% $Li_{0.5}Fe_{2.5}O_4$ composite material phases corresponding to perovskite and spinel lattice of P4mm and Fd-3m space groups have been identified. Whereas for 60% $BaTiO_3$ and 40% $Li_{0.5}Fe_{2.5}O_4$ composite phases corresponding to P4mm ($BaTiO_3$)[9] [COD Number: 1507756], Fd-3m (spinel lattice - $Li_{0.5}Fe_{2.5}O_4$)[10-11] [COD Number: 1541599] and Pbca (Li_5FeO_4) [COD Number: 1542046] space groups have been observed.



Figures 1. X-ray diffraction of pure and lithium ferrite substituted $BaTiO_3$ ferroelectric.

The presence of Li_5FeO_4 phase is very less in the composite material. Proper indexing of (hkl) given for each peak in distinguishing the various phases (Figure 1). The lattice parameters of $BaTiO_3$ and $Li_{0.5}Fe_{2.5}O_4$

for ferroelectric phase and ferrite phase have been calculated using following equations.

$$d_{hkl} = \frac{1}{\sqrt{\frac{h^2+k^2}{a^2} + \frac{l^2}{c^2}}} \text{ for ferroelectric phase and } d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}}$$

for ferrite phase.

Lattice parameter are calculated and tabulated in table 1, shows the consistent decrease in c/a ratio indicating suggesting the incorporating of ferrite in the system without any structural changes.

Table 1. Structural properties of lithium ferrite-$BaTiO_3$ ferroelectric.

$BaTiO_3$(BT)+ $Li_{0.5}Fe_{2.5}O_4$ (LF)	**LATTICE PARAMETER $BaTiO_3$**		**Ratio**	**CELL VOLUME (V) (Å)^3**	**$Li_{0.5}Fe_{2.5}O_4$** a(Å)
	a(Å)	c (Å)	c/a		
$BaTiO_3$(BT)	4.00859	4.04144	1.0081	64.9410	---
80%BT+20%LF	4.00272	4.01226	1.0023	64.2836	8.4306
60%BT+40%LF	4.00710	3.99893	0.9979	64.2101	8.4748

The observed lattice parameters for ferroelectric phase and ferrite phase are in agreement with the reported values.[12]

Figure 2 represents the FTIR spectra for the composites showing the appearance of ferrite peak for higher concentration of ferrite content. Formation of two main peaks located peak at wave number around v_1= 542-529 cm^{-1} and v_2= 410-430 cm^{-1} as ferrite peaks increases with increase in ferrite concentration. The bands at lower frequency are allocated to metal oxygen stretching vibrations at octahedral site and bands at higher frequency are allocated to metal oxygen stretching vibrations at tetrahedral sites. Wave number v_1= 542-529 cm^{-1} attributing to vibrational mode of tetrahedral lattice while v_2= 410-430 cm^{-1} peak is due to octahedral lattice in ferrite system.[13]

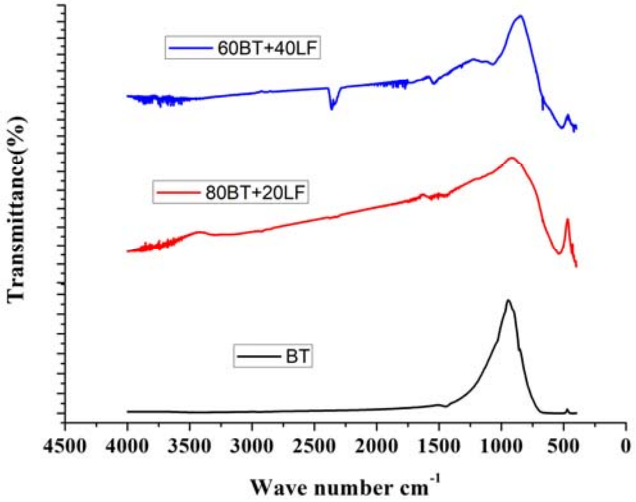


Figure 2. FTIR Spectra of lithium ferrite-$BaTiO_3$ ferroelectric.

Broadening of octahedral peak at wave number v_2= 410-430 cm^{-1} with ferrite increase suggests the influence of ferrite in the composites. The peak at 470 cm^{-1} observed for all the compositions corresponds to Ti-O bending vibrations which in turn confirms the perovskite structure of $BaTiO_3$. In case of 60% $BaTiO_3$ and 40% $Li_{0.5}Fe_{2.5}O_4$ composite a peak at 669 cm^{-1} has been observed which can be related to Li_5FeO_4 phase.[14]

Dielectric permittivity spectra measured for composite samples for wide frequency range (<3 GHz) is shown in the Figure 3. Large value of dielectric constant decreases with increase in ferrite content that is shown in the figure indicates the heterogeneity nature in the composites where each ferroelectric grain is surrounded by ferrite grain. From the figure, it can be noted that dielectric value decreases with increase in frequency for high BT content sample whereas it shows stability in broad frequency range and then shows dispersion beyond 600 MHz. The relaxation shift is clearly observed for higher ferrite content. It is well known that, dielectric constant (ε) decreases with increase in frequency as contribution ceases with dipoles which are unable to pursue the applied field showing dispersion at high frequency. Dispersion regions observed are governed by conductivity nature as suggested by Maxwell-Wagner.[15-17] Effect of ferrite content that is shown clearly in the Figure 4 suggests, fewer number of dipoles following the direction of electric field that shorten the interfacial polarization curtailing dielectric constant.[18] Even though high dielectric nature was observed in the composites due to nature of barium titanite, interaction of dipoles or electron relaxation mode coupling is also seen.[19]

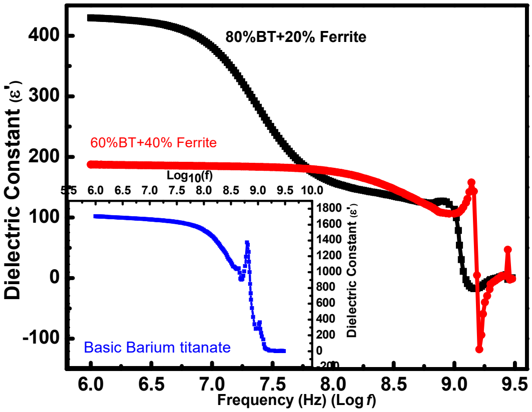


Figure 3. Dielectric constant variation of lithium ferrite-$BaTiO_3$ ferroelectric.

Investigation of temperature dependence of the dielectric nature of composite samples at lower frequency (10 kHz) is shown in Figure 4. Occurrence of transition peak with increase in ferrite content is evident from the figure. As per case of normal ferroelectrics, dielectric value in $BaTiO_3$ increases with increase in temperature and transition peak is observed at 130°C at which dielectric value decreases. Sharp defined value of dielectric obeys Curie-Wiess law for $BaTiO_3$, shows normal behavior, indicating the transition from tetragonal to cubic structure. Figure 4 shows that the dielectric constant increases with increase in temperature in all samples. Transition peak shifts towards higher temperature region in composite samples with increase in ferrite concentration. Shift of transition peak also reform the Curie temperature towards high temperature region with increased ferrite concentration, as reported elsewhere.[20] With increase in ferrite content (at x=0.20), T_c peak is observed to be suppressed, showing the ferrite phase behavior in the dielectric nature. With further increase in ferrite content (x=0.40), an extended rise in dielectric value is observed in the plots. High dielectric values observed at low frequencies in high temperature conditions could be due to either space charge polarization effect at ferroelectric-ferrite interface or conducting mechanism, which are prevalent in the ferrites.[21-23] Sudden increase of dielectric constant can be attributed to thermal excited charges, which hop due to polarization.[21]

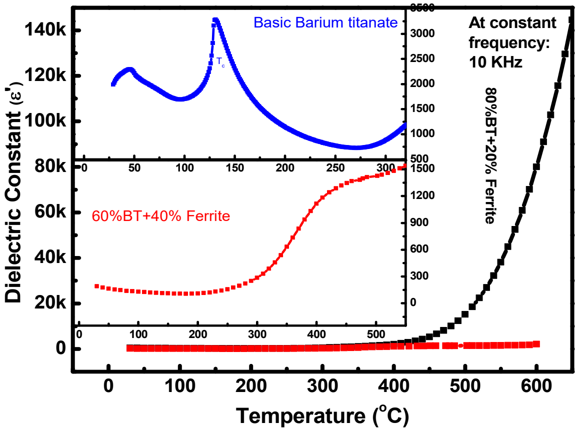


Figure 4. Temperature dependent dielectric constant for lithium ferrite-$BaTiO_3$ ferroelectric.

Conclusions

Dependence of dielectric constant on the frequency and temperature for varying ferrite content in ferroelectric composites investigated. Dielectric constant decreases with increase in ferrite content in composite samples in its frequency range, showing usual dispersion behavior. Lower dielectric values were understood, on the basis of diminishing interfacial polarization, which decreases with increase in ferrite content. Curie temperature also increases with increase in ferrite content in composite samples.

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