

## **5.1. Introduction**

In the past few years, the science and technology of nano materials have been expeditiously progressing. The improvement of various synthesis routes has many challenges in terms of the control of size and shape of nano dimension materials by commute the synthesis procedures [Jie *et al.* (2004), Patrinoiu *et al.* (2012)]. High dielectric permittivity materials have very important in the miniaturization of electronic communication devices and obtain this requirement the integration and packaging techniques. In recent years, this has been increasing desire in flexible, high dielectric constant particulate composites made of a ferroelectric ceramic and a polymer for use in high-density energy storage and capacitance-based components like capacitors, resonators and filters [Bai *et al.* (2000), Kuo *et al.* (2001)]. Subramanian *et al.* (2000), has observed first high dielectric constant in CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> (CCTO) ceramic due to the formation of internal barrier layer capacitances at twin boundaries. CCTO ceramic has a single-step internal barrier layer capacitor where insulating grain boundaries divide the semiconducting grains. It has been given much consideration, not only because of the numerous potential technological applications of the materials with such properties but also because of the origin of the giant dielectric constant. It shows interesting unusual physical properties and exhibits the extremely high dielectric constant ( $10^4$ ) which is independent of frequency and temperature (100-500 K) [Ramirez *et al.* (2000), Sinclair *et al.* (2002), Adams *et al.* (2006), Cohen *et al.* (2003), Lunkenheimer *et al.* (2004)]. CCTO-like compounds have general formula ACu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> (A= Bi<sub>2/3</sub>, Y<sub>1/2</sub>, La<sub>2/3</sub>.) have not been extensively studied. Bi<sub>2/3</sub>Cu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> (BCTO) ceramic also has high dielectric constant which is isostructural with CCTO, has been reported [Fang *et al.* (2004), Liu *et al.* (2004), Yang *et al.* (2015)].

Recently, much attention has been focused on lead-free bismuth titanate Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> (BTO) which is ferroelectric materials with a layered structure and belong to the Aurivillius family and has good electrical and electrochemical properties [Ahn, *et al.* (2009)]. In the recent past the lead zirconate titanate, Pb(Zr,Ti)O<sub>3</sub> (PZT) have received much attention among the researchers. The lead-based materials are not good for health which evaporated at high temperature during the preparation of ceramic resulting major problem in an environment in long term. In addition, there is also a volition to limit the unification of lead containing compounds into electronic products and hence, bismuth based layered ferroelectrics may be a more environment friendly. So, there is an increasing requirement to replace lead based material and produces a new lead free material. Lead-free bismuth layer-structured ferroelectric thin films, such as SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> (SBT) and BTO have been intensively studied because of their better strain resistance on common Pt electrodes [Park *et al.* (1999)]. Therefore, as a strain-free material SBT is confined in the usual application due to its small polarization and high processing temperature [Lettieri *et al.* (2000), Lee *et al.* (2000)]. La-doped BTO is more interesting, it is not only crystallized at low processing temperature but it is also relevant with Si-based integrated circuit technology.

In the present manuscript, we have reported the synthesis of 0.5 Bi<sub>2/3</sub>Cu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> - 0.5 Bi<sub>3</sub>LaTi<sub>3</sub>O<sub>12</sub> (BCLT-55) nano-composite using the metal nitrate in solution form and solid TiO<sub>2</sub> in the semi-wet route. This preparation route shows the improvement in dielectric, ferroelectric and magnetic properties. The composite has been characterized by XRD, SEM, AFM and TEM analysis. The purpose of the present work is to investigate the electrical and magnetic properties of the BCLT-55 composite using non ferroelectric BCTO and ferroelectric BLTO materials.

## **5.2. Experimental**

The nano-composite 0.5 Bi<sub>2</sub>/3Cu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub>-0.5 Bi<sub>3</sub>LaTi<sub>3</sub>O<sub>12</sub> (BCLT-55), was prepared by the semi-wet route using few steps. Firstly, Bi<sub>2</sub>/3Cu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> ceramic material synthesized by semi-wet route using bismuth nitrate, Bi(NO<sub>3</sub>)<sub>3</sub>.5H<sub>2</sub>O (99.5%; Merck, India), copper nitrate, Cu(NO<sub>3</sub>)<sub>2</sub>.3H<sub>2</sub>O (99.8%; Merck, India), and titanium oxide, TiO<sub>2</sub> (99.9%; Merck, India), were taken in their stoichiometric ratio. A Solution of Bi(NO<sub>3</sub>)<sub>3</sub>.5H<sub>2</sub>O and Cu(NO<sub>3</sub>)<sub>2</sub>.3H<sub>2</sub>O were prepared by using distilled water. Both the solution was mixed together in a beaker. Solid TiO<sub>2</sub> was added in the solution and calculated amount of citric acid, C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>.H<sub>2</sub>O (99.5%; Merck, India), equivalents to metal ions was dissolved in distilled water and mixed with the solution. The resulting solution was heated on a hot plate at 70-80 °C with continuous stirring to evaporate water. After evaporation of all water, a fluffy gel was formed which burned with the sooty flame. The resulting material was grind using agate-mortar to make it a fine powder. The BCTO dry powder was calcined at 800 °C for 6 h in the muffle furnace. Secondly, Bi<sub>3</sub>LaTi<sub>3</sub>O<sub>12</sub> ceramic was also synthesized by semi-wet route using bismuth nitrate, Bi(NO<sub>3</sub>)<sub>3</sub>.5H<sub>2</sub>O (99.5%; Merck, India), solid lanthanum oxide, La<sub>2</sub>O<sub>3</sub> (99.0%; Merck, India), and solid titanium oxide, TiO<sub>2</sub> (99.9%; Merck, India), C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>.H<sub>2</sub>O (99.5%; Merck, India), were taken in their stoichiometric ratio. Calculated amount of citric acid per equivalent to metal ions was added. The synthesis method of BLTO was same as BCTO ceramic. Thirdly, an appropriate amount of prepared powders of BCTO and BLTO were mixed with ethanol and grind for 24 h to make a uniform dispersion of the composite. The resulting ceramic was dried at 120 °C for the 4 h in the hot air oven. This powder was used to make cylindrical pellets (11.5 mm x 1.00 mm) on applying 5 tons of pressure using 2-3 drops of 2% poly vinyl alcohol (PVA) as a binder.

The pellets were heated to 500 °C for 2 h to remove the binder. The resulting BCLT-55 composite pellets were sintered at 900 °C for 8 h.

The crystalline phase of the sintered pellet was identified by X-ray diffractometer (Rigaku miniflex 600, Japan) using Cu-K $\alpha$ , as X-ray source with a wavelength of 1.54 Å. The particle of the composite was examined using a transmission electron microscope (TEM, FEI TECANI G<sup>2</sup> 20 TWIN, USA). Specimens for TEM analysis were prepared by dispersing the sintered BCLT-55 composite powders in acetone by ultra-sonication. The found suspensions were deposited onto the carbon-coated copper grid and dried for 3 h in hot air oven. The micro structures of the composites were examined by using a scanning electron microscope (ZEISS, model EVO-18 research; Germany). The elemental analysis of the sintered pellet of BCLT-55 was carried by EDX (Oxford instrument; USA) attached with SEM. The surface morphology and thickness of BCLT-55 composite was examined using atomic force microscopy (NTEGRA Prima, Germany). The ferroelectric hysteresis loops were obtained by using ferroelectric tester (Automatic PE loop Tracer Marine India). For magnetic measurement, a Quantum Design MPMS-3, (Magnetic property Measurement System) was used over a temperature range 2–300 K and applied a magnetic field of 7 tesla. In addition, the temperature dependent magnetic moments were measured in the temperature range of 2-300 K under field cooling (FC) and zero field cooling (ZFC) condition. The temperature variation of field cooled (FC) and zero field cooled (ZFC) magnetization at 100 Oe applied field were carried out using SQUID VSM dc magnetometer. The dielectric and electrical properties of the BCLT-55 composite was measured using an LCR meter (PSM 1735, NumetriQ 4<sup>th</sup>Ltd.U.K.) with the variation of frequency (10 Hz - 5 MHz) at the room temperature (300 – 500 K). In order to perform the

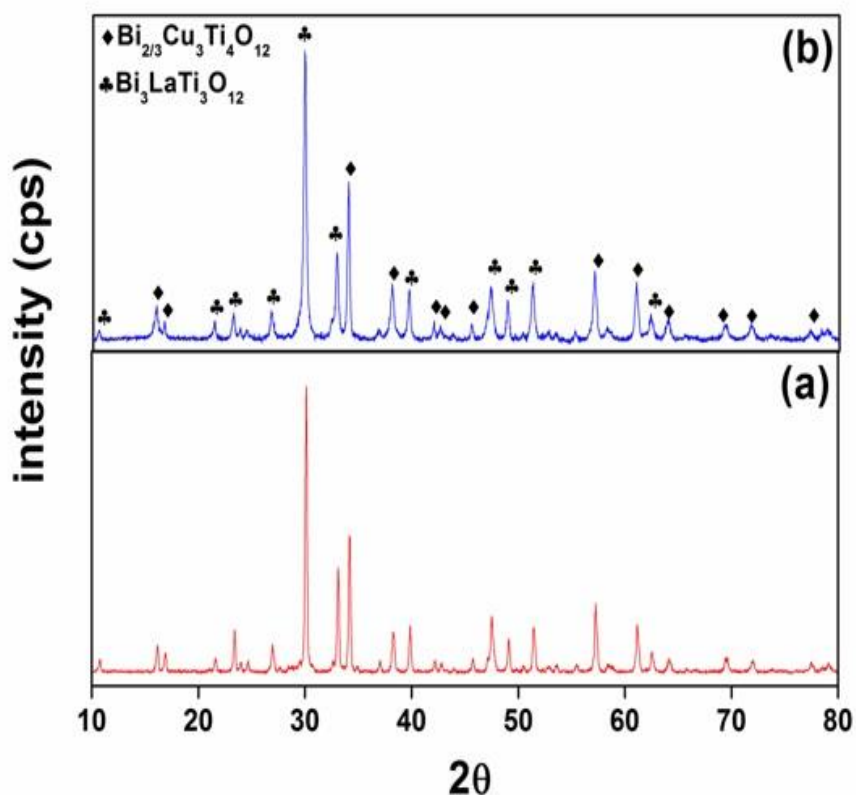
electrical measurements, the silver paste was coated on both sides of the circular faces of the pellet dried at 50 °C for 30 min.

### 5.3. Results and discussion

#### 5.3.1. Microstructural studies

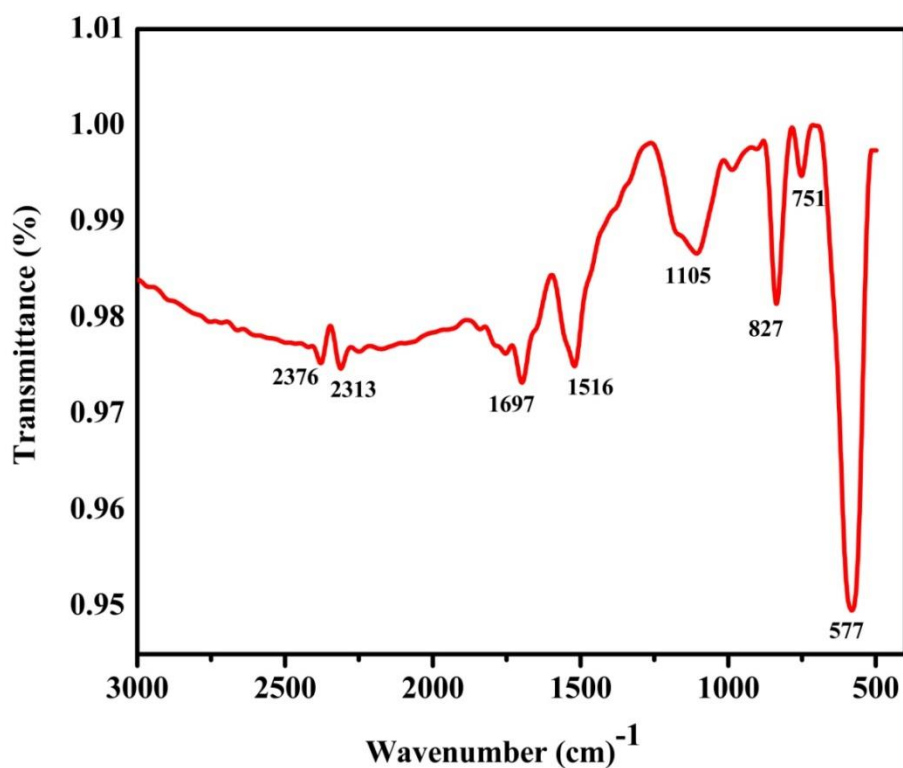
Fig.5.1 shows XRD patterns of the BCLT-55 composite calcined at 800 °C for 6 h and sintered at 900 °C for 8 h. It is observed from the XRD pattern that in the composite BCTO and BLTO phases are present (JCPDS 50-0278, 80-1343). XRD data is used to determine the average crystallite size given by the Scherrer formula.

$$D = k\lambda/\beta \cos \theta \quad (5.1)$$



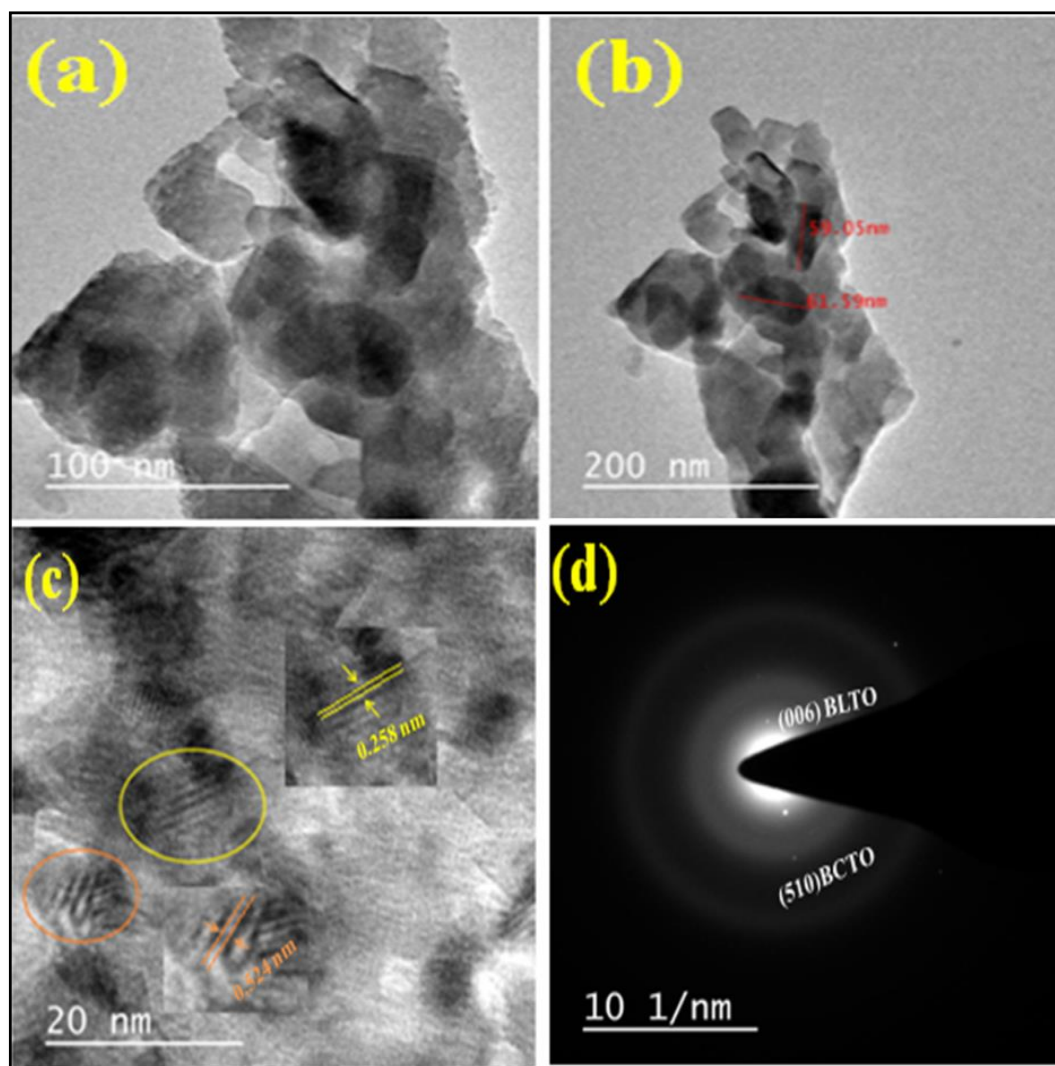
**Fig.5.1. XRD patterns of BCLT-55 composite (a) calcined at 800 °C for 6 h and (b) sintered at 900 °C for 8 h.**

where  $D$  is the crystallite size,  $\lambda$  is the wavelength of the X-ray,  $k$  is a constant taken as 0.89,  $\theta$  is the Bragg angle of the peaks, and  $\beta$  is the full width at half maximum (FWHM) of peaks. The peak broadening due to the instrument was corrected with the data of the standard sample. In the single-line analysis method, the Cauchy component of the Voigt function represents the crystallite size. The crystallite size of BCLT-55 composite was calculated by using corrected value of  $\beta$  in the above equation. The average crystalline size of the composite was found to be  $50 \pm 5$  nm. Fig.5.2 shows the FT-IR spectrum of BCLT-55 composite calcined powder at 800 °C for 6 h. The peak observed at 577, 751 and 827  $\text{cm}^{-1}$  explained the Ti-O-Ti, Ti-O and Cu-O bands.



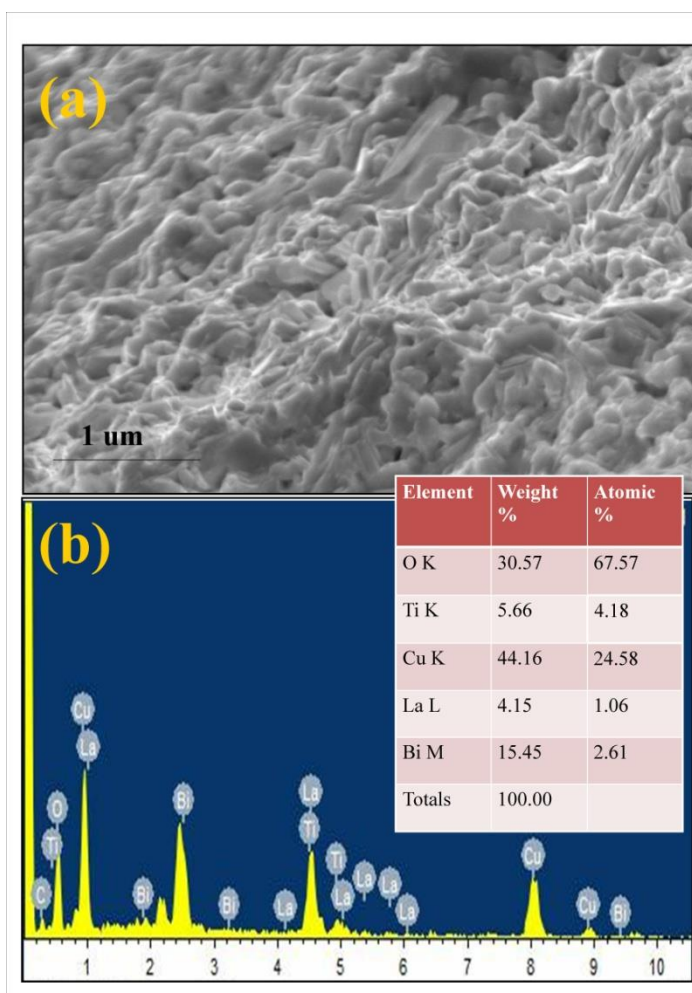
**Fig.5.2. FTIR spectra for the BCLT-55 composite calcined at 800 °C for 6 h.**

The O–H stretching vibration mode shows the absorbed water molecule (at 1516 and 2376  $\text{cm}^{-1}$ ) [Ocwelwang *et al.* (2014)]. The peaks in the 1105  $\text{cm}^{-1}$  frequency region for calcined powder are attributed to the nitrate bands [Simoes *et al.* (2006), He *et al.* (2006)]. Fig.5.3 shows transmission electron microscopy (TEM) images of the BCLT-55 nano composite. The shape and the size of the nano particles of the composite were not uniform.



**Fig.5.3.(a & b) shows TEM micrographs of BCLT-55 composite sintered at 900 °C for 8 h, (c) presents a high resolution TEM micrograph of the BCLT-55 interface and (d) SAED pattern of BCLT-55 composite.**

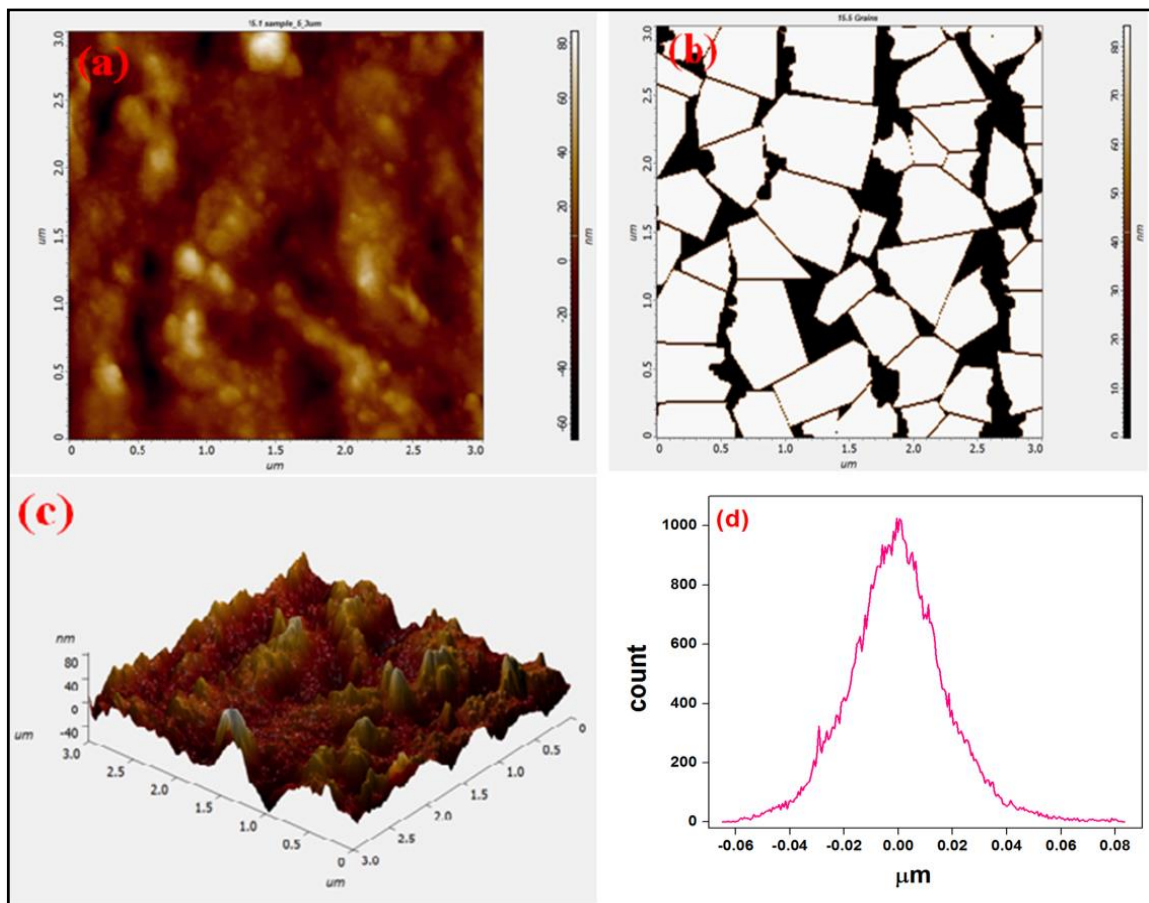
The size distributions of the particle were found to be in the ranges of  $55 \pm 3$  nm. The average particle size calculated from the XRD peak substantiates the result obtained by TEM analysis. Fig.5.3(c) shows the high-resolution TEM analysis (HRTEM) of BCLT-55 nano composite. In this figure, distinct parallel lines were observed at two different places. The distance between two parallel lines indicates inter-planer distance (**d**). The values of **d** were found to be 0.524 and 0.258 nm. The **d** value of 0.524 and 0.258 nm was matched with a plane (1 1 0) of BCTO and plane (2 0 4) of BLTO ceramic respectively. These result also supported by XRD study.



**Fig.5.4. (a) SEM images (b) EDX spectra corresponding to BCLT-55 composite sintered at 900 °C for 8 h.**



Fig. 5.3(d) shows the selected area electron diffraction (SAED) of BCLT-55 composite. The presence of rings patterns in the SAED supporting the formation of nano composite. Fig. 5.4(a) shows the SEM micrograph of BCLT-55 composite sintered pellets at 900 °C for 8 h, respectively. It clearly shows the formation of composite and no separated grains were observed. Fig. 5.4(b) shows electron diffraction X-ray spectroscopy (EDX) pattern of the composite.

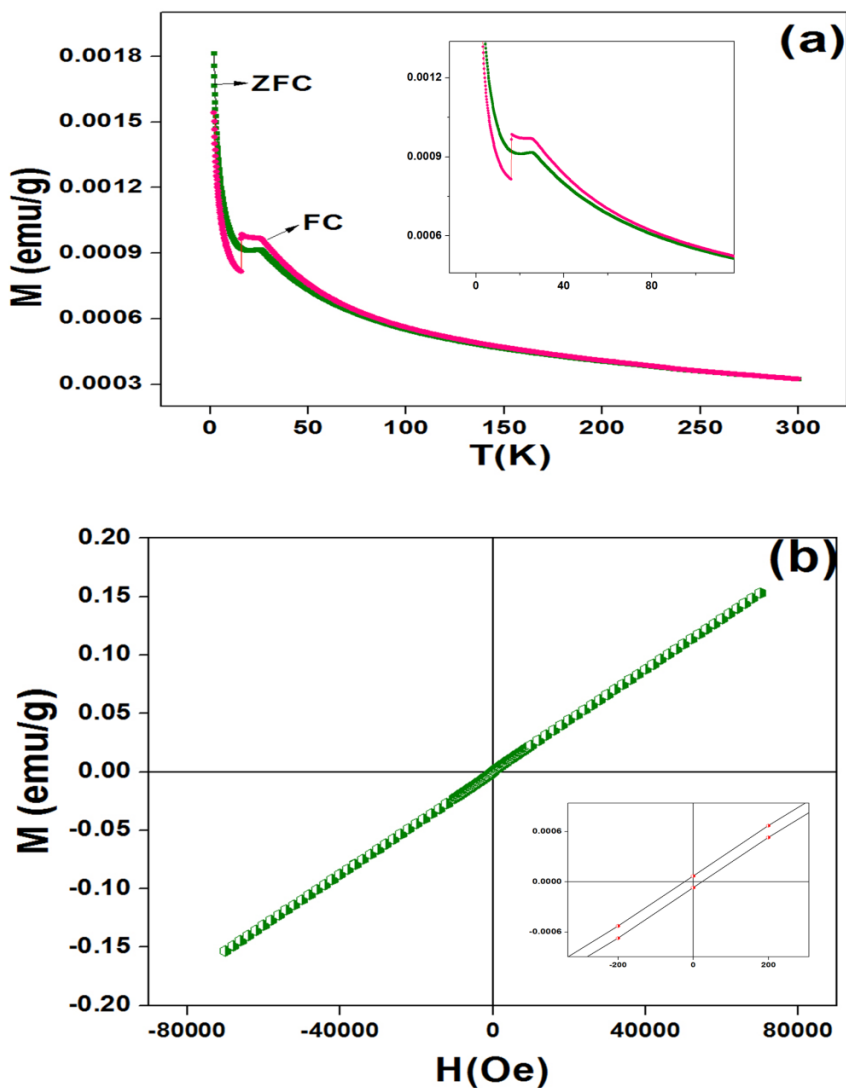


**Fig.5.5. AFM images of BCLT-55 composite sintered at 900 °C for 8 h, (a&b) two-dimensional image showing grains and grain-boundaries, (c&d) three-dimensional image and histogram curve shows roughness of grain.**

The quantitative composition of the composite was obtained from EDX data as shown as in the inset figure. The atomic percentage and weight percentage of Bi, La, Cu, Ti and O were found to be 2.61, 1.06, 24.56, 4.18, 67.57 and 15.45, 4.15, 44.16, 5.66, 30.57 respectively. The observed atomic percentage of the elements is exactly matched to our initial experimental data which confirmed the purity of the composite. Fig.5.5 shows the two-dimensional AFM image of BCLT-55 composite sintered at 900 °C for 8 h. Fig.5.5 (a) shows AFM image of the fractured surface with heterogeneous grain while Fig.5.5(b) shows the clear grain boundaries with a heterogeneous grain size of the composite. The maximum profile valley depth of two-dimensional structures was found to be 54.702 nm. The root mean square roughness, average roughness and maximum area peak height were found to be 18.297, 14.000 and 84.086 nm estimated for a three-dimensional image of Fig. 5.5(c). Fig. 5.5(d) was defining the roughness of grains for the three-dimensional structure of BCLT-55 composite [Khare *et al.* (2016)].

### **5.3.2. Magnetic properties**

Fig.5.6 (a) shows the magnetization curve of 0.5 Bi<sub>2</sub>/3Cu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> - 0.5 Bi<sub>3</sub>LaTi<sub>3</sub>O<sub>12</sub> (BCLT-55) composite as a function of temperature. The hysteresis loop of the BCLT-55 composite was observed at an applied field of 100 Oe with zero-field cooling (ZFC) and field cooling (FC) curve at the temperature 2-300 K. It is observed from the figure that ZFC and FC decrease with increasing temperature. The ZFC and FC curves overlapped above 80 K as clearly shows in an inset. Both curves show broad peaks at 25 K with increasing magnetization. This behavior of the composite may be exhibited to magnetic transition from paramagnetic to anti ferromagnetic.



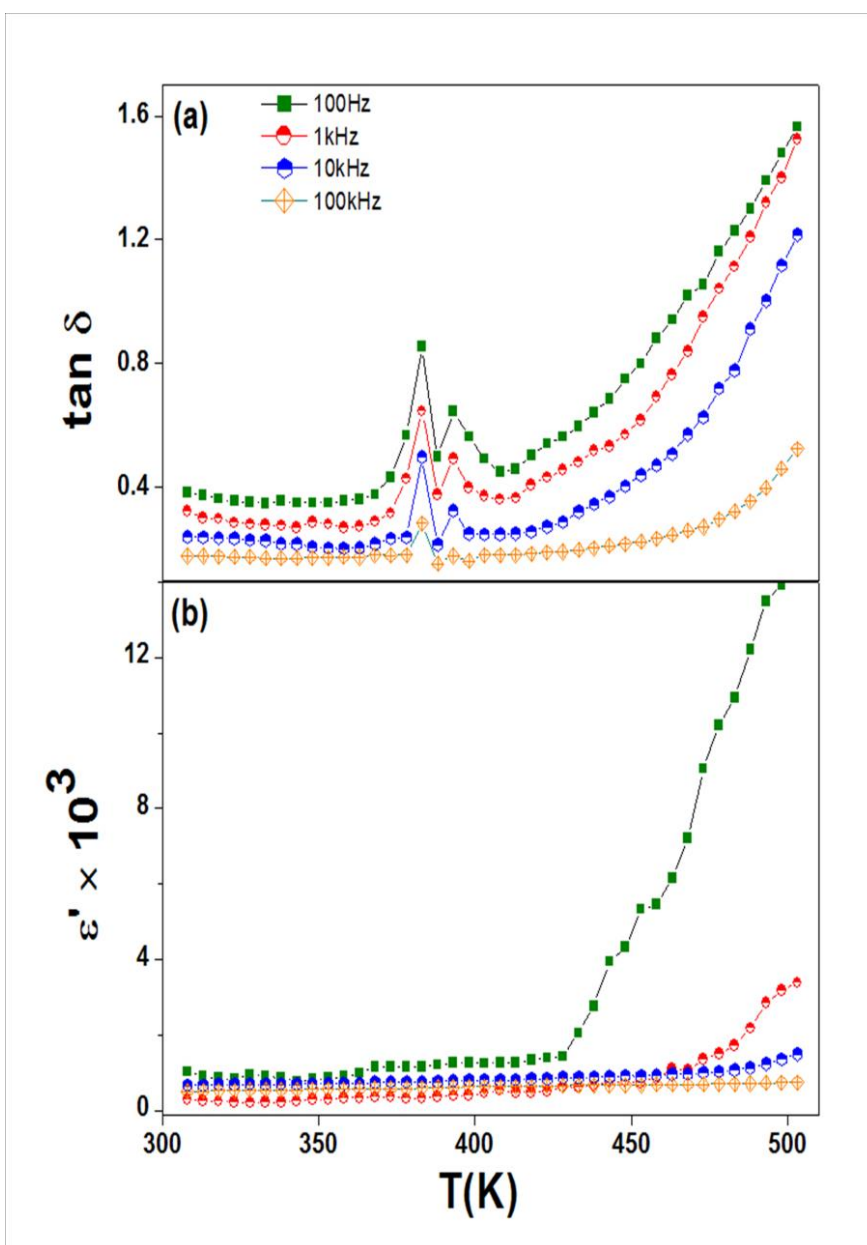
**Fig.5.6.(a)** Temperature-dependent zero field cooled (ZFC) and field cooled (FC) magnetization measured at H=100 Oe, **(b)** magnetization versus applied field at 300 K for the BCLT-55 composite.

This transition temperature is known as the Neel temperature. The FC curve was suddenly breakdown at 16 K with magnetic moment  $9.850 \times 10^{-4}$  -  $8.169 \times 10^{-4}$  emu/g and decreases with increasing temperature. Fig.5.6(b) shows the variation of magnetization as a function of

applied field  $\pm 7$  tesla. The M-H curves of BCLT-55 composite show linear and unsaturated in nature. However, the hysteresis loop is observed in zoom view at a low magnetic field as shown in the inset, which confirms the anti ferromagnetic structure and weak ferromagnetic moment. The coercivity value was found to be 14 Oe [Lei *et al.* (2014)]. The low value of coercivity was indicating the BCLT-55 composite as soft magnetically materials. The composite may be used in transformer, inductor cores, recording heads, microwave devices and magnetic shielding.

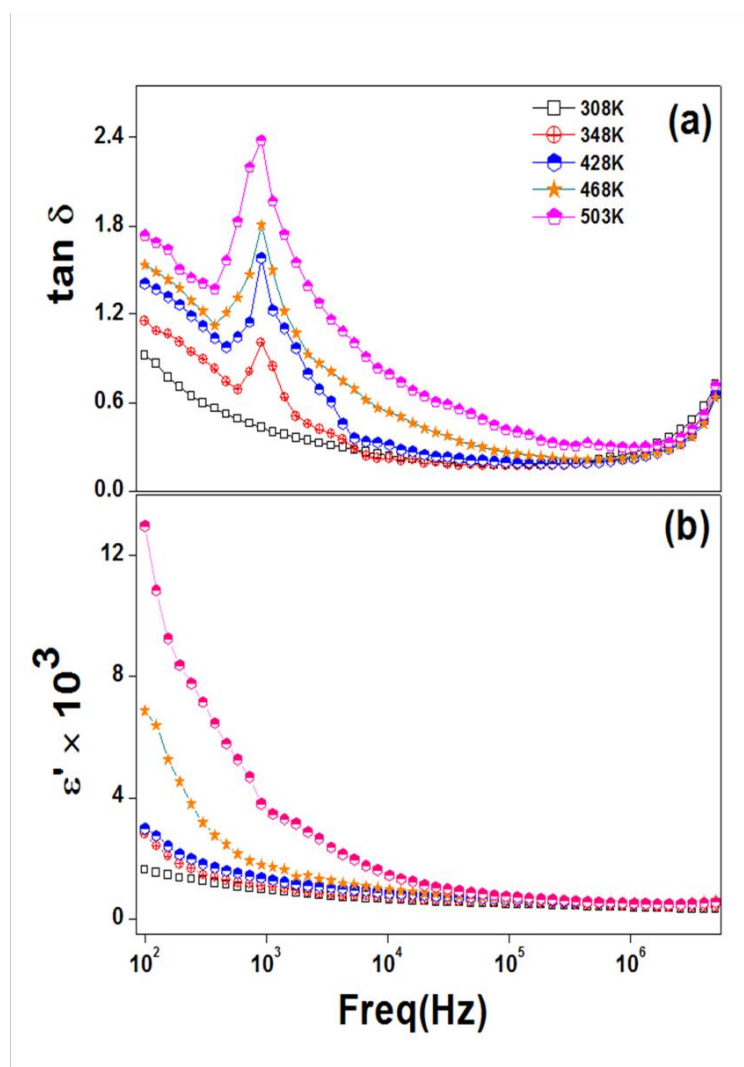
### **5.3.2. Dielectric Behavior**

Fig.5.7 shows the variation of dielectric loss ( $\tan \delta$ ) and dielectric constant ( $\epsilon'$ ) with temperature for the BCLT-55 composite at few selected frequencies. It is observed that the value of  $\tan \delta$  increases with increasing temperature from 300 to 500 K (Fig.5.7a). The relaxation peaks were observed in the composite material at 383 K for all measured frequency. The value of  $\tan \delta$  for composite was found to be 0.3, 0.3, 0.2 and 0.1 at 100 Hz, 1 kHz, 10 kHz and 100 kHz, respectively, at 308 K which remains constants up to 368 K. The occurrence of relaxation peaks in the composite is due to the presence of space charge polarization in the ceramic [Singh *et al.* (2014), Singh *et al.* (2011), Norezan *et al.* (2012), Yu *et al.* (2008)]. Fig.5.7(b) shows an increase of dielectric constant of composite with temperature from 425 - 500 K and remains almost constants from 300 - 425 K. The value of dielectric constant ( $\epsilon'$ ) of the composite was found to be  $0.73 \times 10^3$ ,  $13.94 \times 10^3$  at 100 kHz and 100 Hz respectively at 498 K [Fang *et al.* (2006), Warangkanagool *et al.* (2012)]. It is also observed from the figure that dielectric constant and dielectric loss decrease with increasing frequency.



**Fig.5.7.** Plot of (a) tangent loss ( $\tan \delta$ ) and (b) dielectric constant as a function of temperature for BCLT-55 composite sintered at 900 °C for 8 h.

Fig.5.8 shows the variations of dielectric loss ( $\tan \delta$ ) and dielectric constant of the composite as a function of frequency from  $10^2$  to  $10^6$  Hz at few selected temperature. Temperature dependent dielectric relaxation peaks were observed. On increasing temperature peaks shifted to low frequency region (Figure 5.8a) which substantiate the presence of Debye- type relaxation in the composite.



**Fig.5.8. Plot of (a) tangent loss ( $\tan \delta$ ) and (b) dielectric constant as a function of frequency for BCLT-55 composite at few selected temperatures.**

It is also observed that relaxation is absent at room temperature. It is observed from the Fig.5.8(b) that dielectric constant decreases with increasing frequency. This is the general trend for the materials. The value of dielectric constant at 503 K was found to be  $12.9 \times 10^3$  at 100 Hz whereas at room temperature it was  $1.62 \times 10^3$ . The high value of dielectric constant at lower frequency region is due to the presence of interfacial space charge polarization [Yadava *et al.* (2016)]. On increasing temperature, the density of charge carrier increases at the interface of grains and grain boundaries resulting high dielectric constant.

#### **5.4. Conclusion**

A nano-composite of 0.5 Bi<sub>2</sub>/3Cu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> - 0.5 Bi<sub>3</sub>LaTi<sub>3</sub>O<sub>12</sub> was synthesized by a semi-wet route using high purity chemicals in a stoichiometric ratio. The phase formation of 0.5 Bi<sub>2</sub>/3Cu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> - 0.5 Bi<sub>3</sub>LaTi<sub>3</sub>O<sub>12</sub> was confirmed by XRD in the composite. The particle size determined by XRD and TEM was found to be  $50 \pm 5$  nm. SEM morphology shows no separate grains of BCLT-55 in the composite structure. The atomic percentage of the elements obtained by EDX data is matched to our initial experimental data which confirmed for a purity of composite. For the AFM study root mean square roughness and average roughness were found to be 18.297 and 14.000 nm respectively. The Magnetic behavior for the BCLT-55 composite revealed anti ferromagnetic with a weak ferromagnetic moment and shows soft magnetically materials. The high value of dielectric constant ( $\epsilon' = 13.94 \times 10^3$ ) of the composite may be explained due to the presence of space charge polarization at the interface.