SYNTHESIS AND CHARACTERIZATION OF Cu–DOPED BaTiO₃

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Abstract:- The research presents a comparative study of the effect of Cu on the Structural transitions properties of $BaTiO_3$. Investigation were carried out on sample of x=0.1-0.3 The chemical formula for Barium Titanate is $BaTiO_3$. As a powder it is white to grey in colour and has a perovskite structure. $BaTiO_3$ the most widely used ferroelectric material. $BaTiO_3$ has a perovskite structure (space group R3c) with chemical formula ABO_3 at Curie temperature ($T_c\sim 120°C$). There is tetragonal structure at room temperature. It is ferroelectric material. Ferroelectrics are crystalline materials that exhibit electrical activity similar to ferromagnets' magnetic behavior. Due to their spontaneous polarization, these materials exhibit spontaneous polarization even in the absence of an external field, and as a result the hysteresis effect. This occurs in ferroelectric materials. up to a given temperature, a certain type of behavior is seen. referred to as Curie's temperature (Tc). This action is not more than this Tc. So far, we have studied and characterized the ferroelectric $Ba_{1-x}Cu_xTiO_3$ by suitable doping compositions of Cu (x = 0.1, 0.2).

The RT-XRD characterization yielded the expected characteristic peaks with some impurity peaks indicates the presence of impurity phases in the system. The Raman peak shifted in Raman Spectrum resulting the expected Raman modes i.e., A, E and Mixed modes A+E at 300K.

Keywords:- Curie temperature, Ferroelectrics, Raman Spectrum, Perovskite structure.

1.Introduction:-The research presents a comparative study of the effect of Cu on the Structural transitions properties of $BaTiO_3$. Investigation were carried out on sample of x=0.1-0.3 The chemical formula for Barium Titanate is $BaTiO_3$. As a powder it is white to grey in colour and has a perovskite structure. $BaTiO_3$ was discovered during World War II in 1944 by T. Ogawa and S. Waku. $BaTiO_3$ the most widely used ferroelectric material. $BaTiO_3$ has a perovskite structure (space group R3c) with chemical formula ABO_3 at Curie temperature ($T_c\sim 120°C$). There is tetragonal structure at room temperature. It is ferroelectric material. Ferroelectrics are crystalline materials that exhibit electrical activity similar to ferromagnets' magnetic behavior. Due to their spontaneous polarization, these materials exhibit spontaneous polarization even in the absence of an external field, and as a result the hysteresis effect. This occurs in ferroelectric materials. up to a given temperature, a certain type of behavior is seen. referred to as Curie's temperature (Tc). This action is not more than this Tc.

1.1. Ferroelectric materials

Ferroelectricity is a characteristic of certain materials that have a spontaneous electric polarization that can be reversed by the application of an external electric field. All ferroelectrics are pyroelectric, with the additional property that their natural electrical polarization is reversible. Ferroelectric materials, for example, Barium titanate are composed of crystals in which the structural units are tiny electric dipole that is, in each unite the centers of positive charge and of negative charge are slightly separated. In some crystals these electric dipole spontaneously line up in clusters the domains, and inferroelectric crystal the domains can be oriented predominantly in one direction by a strong electric field reverses the predominant orientation of ferroelectric

domains, though the switching to a new direction lags somewhat behind the charge in the external electric field. This lag of electric polarization behind the applied electric field is ferroelectric hysteresis.

1.2. Applications of ferroelectric materials

- Capacitors.
- Non-volatile memory.
- Piezoelectric for ultrasound imaging and actuators.
- Electro-optic materials for data storage applications.
- Thermistors.
- Switches known as trans char.

1.3. Perovskite Crystal Structure

A **perovskite** is any material with a crystal structure following the formula ABX_3, which was first discovered as the mineral called perovskite which consists of calcium titanium oxide ($CaTiO_3$). 'A' and 'B' are two positively charged ions(i.e. cations), often of very different sizes, and X is a negatively charged ion (an anion, frequently oxide) that bonds to both cations. The 'A' atoms are generally larger than the 'B' atoms. Perovskite structures are adopted by many oxides that have the chemical formula ABO_3.
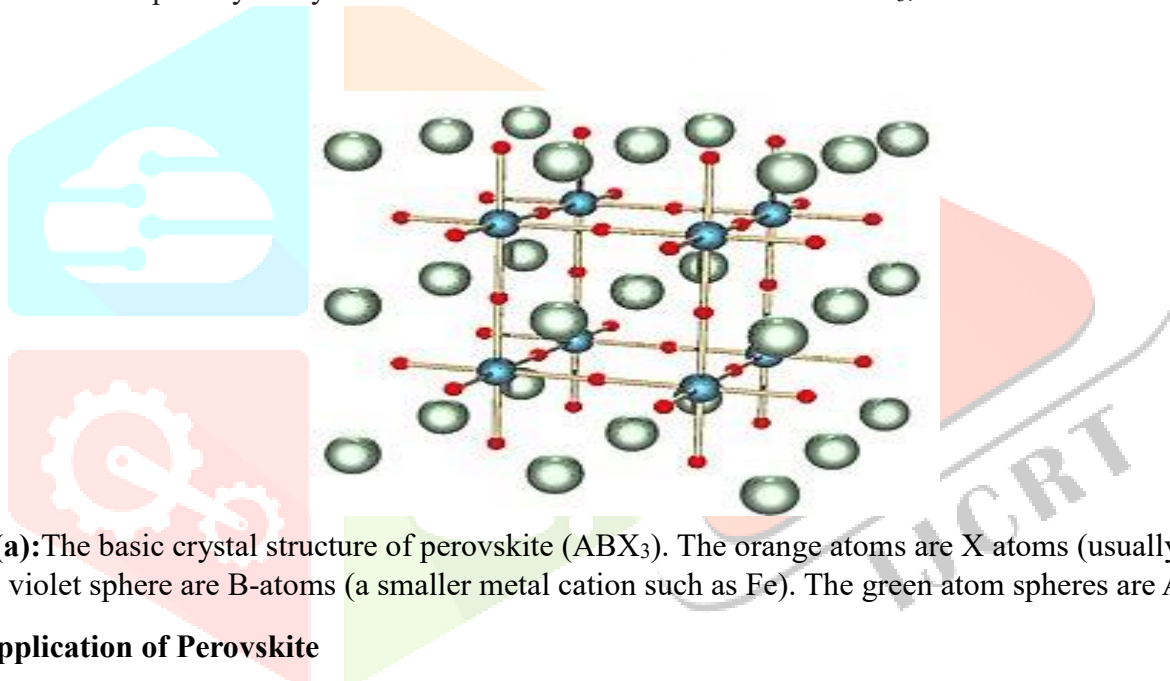

Fig(a): The basic crystal structure of perovskite (ABX_3). The orange atoms are X atoms (usually oxygen), the violet sphere are B-atoms (a smaller metal cation such as Fe). The green atom spheres are A- atoms.

1.4 Application of Perovskite

There are several industries with interest in perovskites applications that are undertaking research to improve the technology. Two industries with particular interest in it are photovoltaics and optoelectronics. It offers a promising alternative to traditional silicon solar cell as they are more tunable and cheaper to manufacture. Its efficiency is high. Perovskite based LED offer the nest generation in this technology. The opto-electronic properties of perovskite materials such as tenability, high photoluminescence quantum yield and cheaper manufacturing have capture the interest of many researchers and technology companies alike.

1.5. BaTiO₃ Structural Phase Transition And Its Structure

Understanding the main differences between the crystalline structures of the polymorphs involved in the phase transition corresponds to an important step on the disclosure of the mechanism involved in such process. Indeed, the connection between different polymorphs is strictly associated with the creation, breaking, or distortion effects regarding the chemical bonds. Thus, four phases were considered for BTO in this study, and the optimized crystal structure for each polymorph is represented in Figure 1A-D.Figure 1A-D illustrates a schematic representation of BTO clusters constituent of cubic, tetragonal, orthorhombic, and rhombohedral structure perovskites, with space group symmetries of Pm3m, P4mm, Amm2, and R3m, respectively.
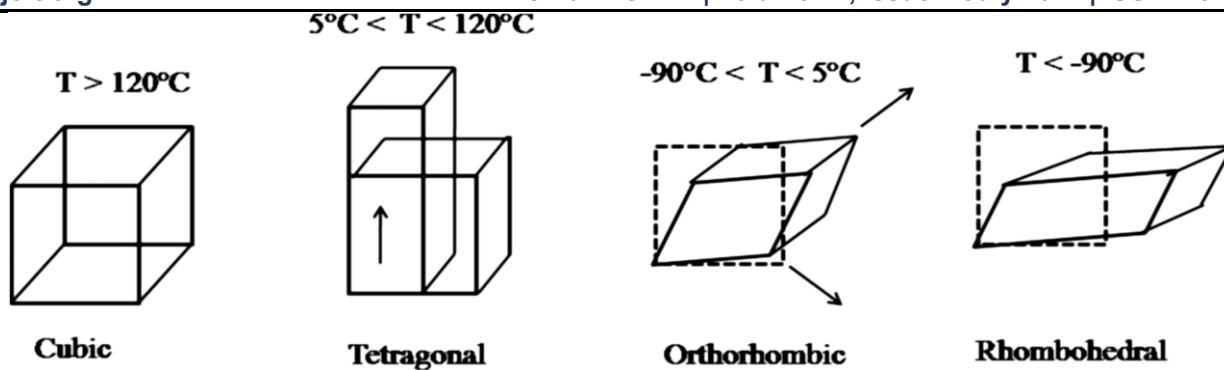
Fig(b): Structure Transition of $BaTiO_3$

The Ti atoms are coordinated to six O atoms in all cases, producing octahedral $[TiO_6]$ clusters (with 6 vertices, 8 faces, and 12 edges). Correspondingly, the Ba atoms are coordinated to twelve O atoms, resulting in $[BaO_{12}]$ clusters (with 12 vertices, 12 faces, and 30 edges). The main difference between BTO cubic and tetragonal phase is a slight displacement in octahedral $[TiO_6]$ clusters with the theta angle from 90 to ~93.3(Figure 1A,B), while orthorhombic and rhombohedral phase results in a theta angle from ~89.8 to ~85.7. Also, such representations are found to be in excellent agreement with the results obtained by Evarestov and Bandura, following the Wyckoff positions of atoms with the site symmetry group .The analysis of the band gap structure and density of the states indicated the bandgap value for the four BTO polymorphs. The band gap is closely related to the difference in the energy level between the valence band VB and conduction band CB, which can be originated from the structural distortion in the materials.
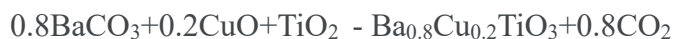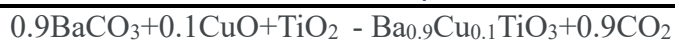
S.N	Temperature	Structure
1.	$120\ ^0C$	Cubic
2.	Room temperature	Tetragonal
3.	$5\ ^0C$	Orthorhombic
4	$-90\ ^0C$	Rhombohedral

1.6. General Doping Concept

The intentional introduction of impurities into a host lattice is the process known as doping, leading to novel phenomena very differently from the precursor materials. The ionic radii of the dopant is the parameter which mainly determine the substitutional site. Ionic radius, dopant concentration, sintering atmosphere all play crucial role. The properties of $BaTiO_3$ thus can be modified through the incorporation with various ions. One of the important application is the change in the magnitude and character of electrical conductivity induced by appropriate dopant.

2.Materials and Methods :

Different experimental probes, including the XRD technique for structural characteristics have been investigated to characterise the produced samples. Different compositions of CuO doped $BaTiO_3$ with $Ba_{1-x}Cu_xTiO_3$ (x = 0.01% to 0.04%) polycrystalline compounds were prepared by solid state reaction method. All the basic ingredients $BaCO_3$, TiO_2 and CuO are analytical reagent grade of Loba Chemi, India with Using the stoichiometric equation $Ba_{1-x}Cu_xTiO_3$ with x = 0.01%, 0.02%, 0.03%, and purity 99.5%, the weights were calculated. 0.04% respectively by using petit electronic balance MK-E series of 0.0001 gm accuracy. Mixed powders with above compositions were hand ground in Agate mortar for 10 hours thoroughly for homogeneity. The homogenous mixtures of all these compositions were then pre-heated for calcination at 900°C in air for 12 hours.

$$0.9BaCO_3+0.1CuO+TiO_2 \text{ - } Ba_{0.9}Cu_{0.1}TiO_3+0.9CO_2$$

$$0.8BaCO_3+0.2CuO+TiO_2 \text{ - } Ba_{0.8}Cu_{0.2}TiO_3+0.8CO_2$$

Fig(c): Agate mortar

Characterizations Techniques

X-Ray Diffraction

X-ray diffraction is a unique method in determination of crystallinity of a compound. XRD is primarily used for

- ID of crystalline material and ID of different polymorphic forms
- Distinguish between amorphous and crystalline material
- Quantification of the percent crystallinity of a sample

XRD analysis is based on constructive interference of monochromatic X-rays and a crystalline sample. The X-rays are generated by a cathode ray tube or by rotating anode method, filtered to produce monochromatic radiation, collimated to concentrate, and direct towards the sample. The interaction of the incident rays with the sample produce constructive interference when condition satisfy Bragg's Law ($n\lambda = 2dsin\Theta$). This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in the crystalline sample. The characteristic X-ray diffraction pattern generated in a typical XRD analysis provides a unique "fingerprint" of the crystal present in the sample .When properly interpreted, by comparison with standard reference patterns and measurements, this finger print allows identification of the crystalline form.

Applications of X-Ray Diffraction
- XRD is non destructive technique
- To identify crystalline phase and orientation
- To determine structural properties; strain, grain size, composition, thermal expansion
- To measure thickness of thin films and multilayer
- To determine atomic arrangement

Raman spectroscopy

It is a spectroscopic technique used to observe vibrational, rotational and low frequency modes in a system of molecule, Raman spectroscopy is commonly used in chemistry to provide a structural finger print by which molecule can be identified it relies on inelastic scattering, or Raman scattering, of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range. The laser light interacts with molecular vibrations, phonons or other excitations in the system, resulting in the energy of the laser photons being shifted up or down. The shift in energy gives information about the vibrational modes in the system. This is a molecular light frequency phenomenon in which a change in frequency occurs .the Raman effect is based on molecular deformations in electric field E determined by molecular polarizability α .The laser beam

can be considered as an oscillating electromagnetic wave with electrical vector E. Upon interaction with the simple it includes electric dipole moment P = αE which deforms molecules. Because of periodical deformation, molecules start vibrating with characteristic frequency γ_m. Monochromatic laser light with frequency γ_0. Excites molecules and transform them into oscillating dipoles. Such oscillating dipoles emit dipole of three different frequencies.
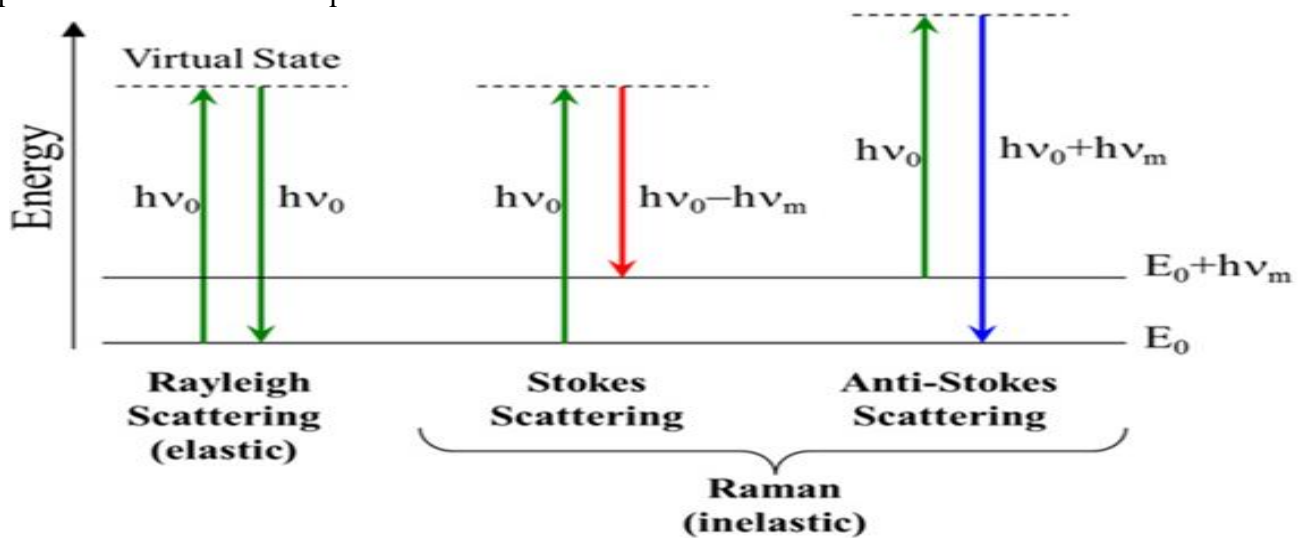
Fig(d): Energy level diagram showing the states involved in Raman spectra

1. A molecule with no Raman active mode absorbs a photon with a frequencies γ_0. The excited molecule returns back to the same basic vibrational state and emits light with the same frequencies as an interaction source. This type of interaction is called an elastic Rayleigh scattering.

2. A photon with frequencies γ_0 is absorbed by a Raman–active molecule, which at the time of interaction is already in the active vibrational state Excessive energy of excited Raman active mode is released. Molecule return to the same vibrational state and the resulting frequency of scattered light goes up to $\gamma_0+\gamma_m$. This Raman frequency is called "antistoke".

3. A photon with frequency γ_0 is absorbed by Raman active molecule which at the time of interaction is in the basic vibrational state. Part of the photon energy is transferred to the Raman –active mode with frequency γ_m and the resulting frequency of scattered light is reduced to $\gamma_0-\gamma_m$. This Raman frequency is called "stokes" frequency .The intensity of stokes line is found to be greater than antistokes line. This can be shown in the figure below.
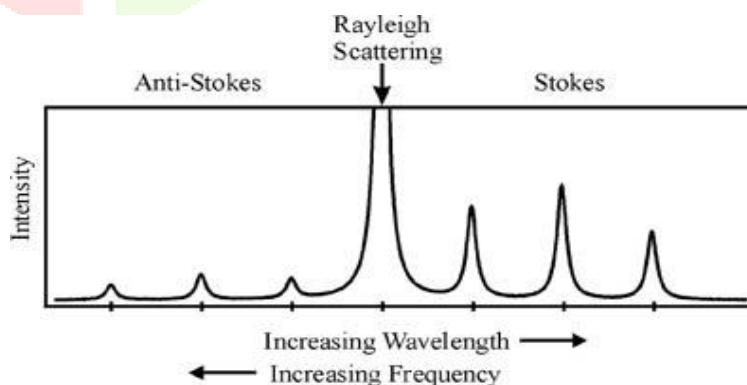

X-Ray Diffraction of $Ba_{(1-x)}Cu_xTiO_3$

 After calcinations these mixtures were examined for their structural studies with X-ray diffraction (XRD) (X-ray diffractometer of make Pan analytical) Cu Kα radiation (λ = 1.541 Å) at room temperature was used for structural studies of these samples. These combined powders were then ground again for an additional hour, granulated with PVA added as a binder, and compressed (at 250 mpa pressure) into pellets measuring 12 mm in diameter and 2 mm in thickness. These pellets were then naturally cooled to room temperature after being

sintered in air for 3 hours at 1100 C. For a smooth and consistent surface, the prepared pellet sample surfaces were polished with carborundum powder. Next, the densities for all pellet-shaped samples were measured.

The X-Ray diffraction characteristics of Cu-doped $BaTiO_3$ are investigated. Fig. 1 shows the room-temperature (RT) X-Ray diffraction (XRD) patterns of $Ba_{1-x}Cu_xTiO_3$ (x = 0.0, 0.1, 0.2). The RT powder XRD measurement were collected from the prepared sample and the crystallinity of the aforementioned compounds was checked using X-Ray diffractometer (Rigaku Smart Lab 9 kW) in θ-2θ mode with the source of Cu K_α having wavelength λ = 1.54Å.
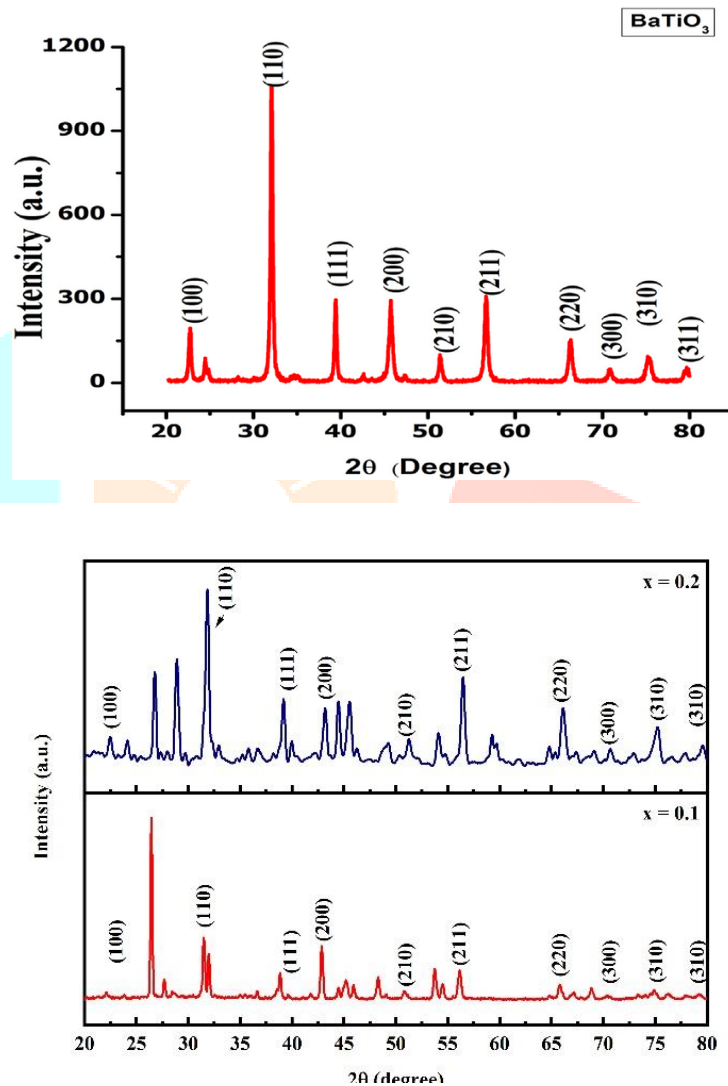
Fig(e):XRD characteristics of $Ba_{1-x}Cu_xTiO_3$ (x = 0, 0.1, 0.2)

From the fig.(e) of XRD pattern of $Ba_{1-x}Cu_xTiO_3$ (x = 0.1), the characteristic peaks (100), (110), (111), (200), (210),(211),(220),(300),and(310) were observed at corresponding 2θ values, respectively. In fig. (e), some of the impurity peaks were identified that corresponds to the different phases present in the system of $Ba_{1-x}Cu_xTiO_3$ (x= 0.1).Similarly, in the XRD pattern of $Ba_{1-x}Cu_xTiO_3$(x=0.2), the characteristic peaks (100),(110),(111),(200),(210),(211),(220),(300),and(310) were observed with some impurity phases (which are unidentified) at corresponding 2θ values, respectively. These obtained peaks for $Ba_{1-x}Cu_xTiO_3$ (x= 0.1, 0.2) are well matched with the pristine Barium titanate.

Raman spectra of $Ba_{(1-x)}Cu_xTiO_3$

The Raman spectrum of Cu-doped Barium titanate was investigated in tetragonal phase. The analysis of Raman spectra in this phase yields is the expected vibrational modes which were found slightly shifted from its pristine one.
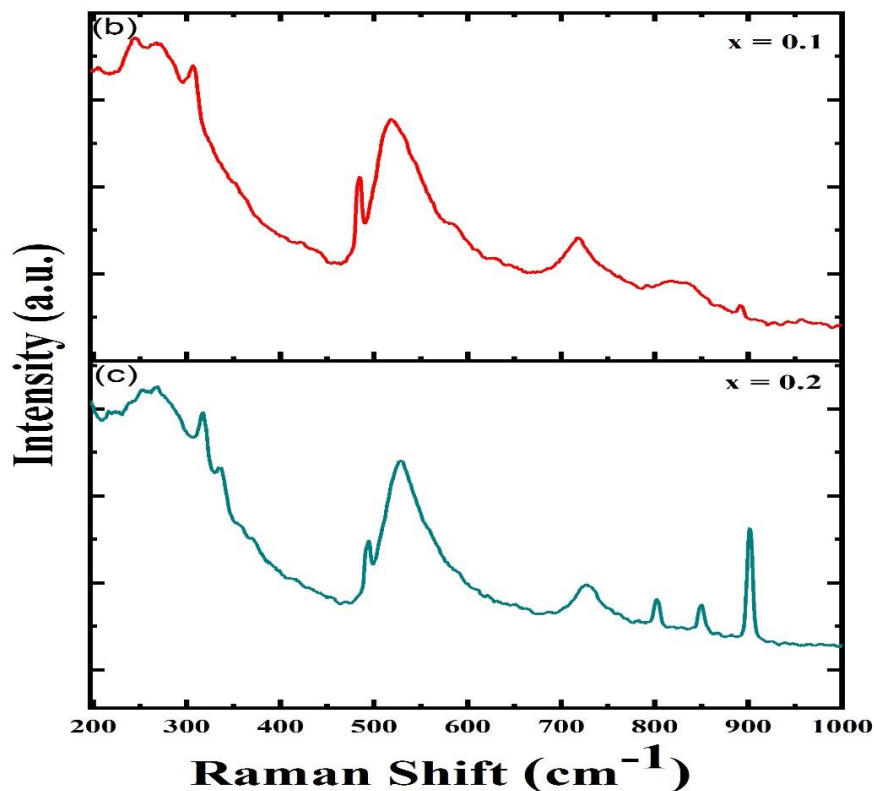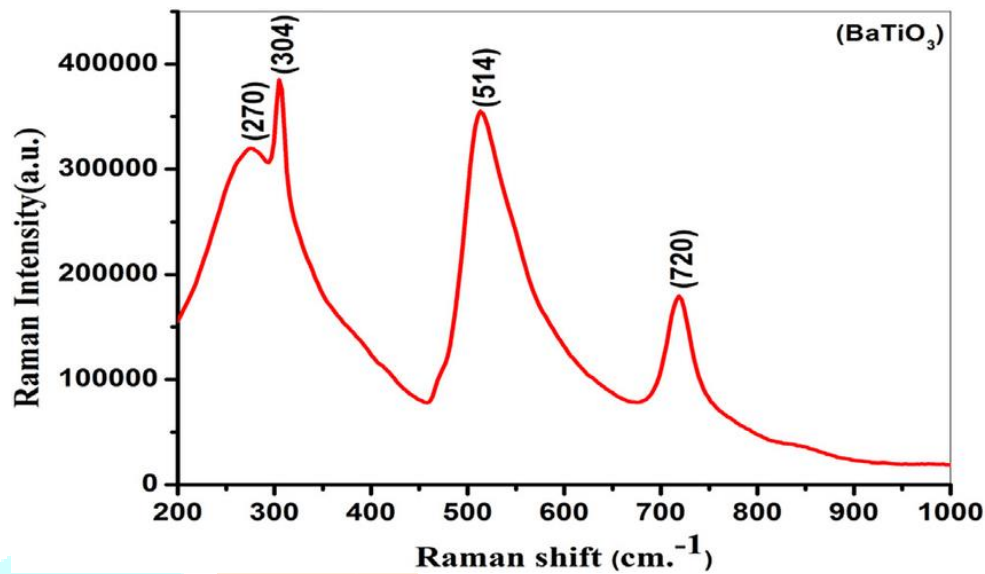

Fig.(f): Raman Characterization of $Ba_{1-x}Cu_xTiO_3$(x=0,0.1,0.2)

From the Fig (f), the expected Raman shift were observed at 257, 306,485, 523 and 730 800 and 900 cm^{-1} for $Ba_{1-x}Cu_xTiO_3$ (x = 0.2). In pristine sample of Barium titanate as mentioned in the literature, the transverse Raman mode A were observed at around 246-270 cm^{-1} and E-transverse and A transverse mode were identified between 303-307, 470 and 512 cm^{-1}, respectively. Further mixed modes (E+A) were observed at 710 cm^{-1}. We have observed that the Raman peaks were found to be shifted from its pristine Raman Shift positions which are reasonably due to the doping composition of Cu in pristine sample $BaTiO_3$.

4. Conclusion:

So far, we have studied and characterized the ferroelectric $Ba_{1-x}Cu_xTiO_3$ by suitable doping compositions of Cu (x = 0.1, 0.2). First of all, we have synthesized the Cu-doped $BaTiO_3$ by conventional solid synthesis method by including the stoichiometric mixtures of powders oxide, grinding, calcinating and sintering process. The RT-XRD characterization yielded the expected characteristic peaks with some impurity peaks indicates the presence of impurity phases in the system. The Raman peak shifted in Raman Spectrum resulting the expected Raman modes i.e., A, E and Mixed modes A+E at 300K.

5. References:

[1] D. Makovec, Z. Samadmija and M. Drofenik, "Solid Solubility of Holmium, Yttrium, and Dysprosium in BaTiO3," Journal of the American Ceramic Society, Vol. 87, No. 7, 2004, pp. 1324-1329. doi:10.1111/j.1151-2916.2004.tb07729.x

[2] D. Maga, P. Igor and M. Sergei, "Influence of Impurities on the Properties of Rare-Earth-Doped Barium-Titanate Ceramics," Journal of Materials Chemistry, Vol. 10, No. 4, 2000, pp. 941-947. doi:10.1039/a909647g

[3] J. Zhi, A. Chen, Y. Zhi, P. M. Vilainho and J. L. Batptista, "Incorporation of Yttrium in Barium Titanate Ceramics," Journal of the American Ceramic Society, Vol. 82, No. 5, 1999, pp. 1345-1348.

[4] Y. P. Pu, W. H. Yang and S. T. Chen, "Influence of Rare Earths on Electric Properties and Microstructure of Barium Titanate Ceramics," Journal of Rare Earths, Vol. 25, Suppl. 1, 2005, pp. 154-157. doi:10.1016/S1002-0721(07)60546-8

[5] L. E. Cross, "Ferroelectric Ceramics: Materials and Application Issues," Ceramic Transactions, Vol. 68, 1996, pp. 15-55.

[6] V. Dharmadhikari and W. Grannemann, "Photovoltaic Properties of Ferroelectric BaTiO3 Thin Films rf Sputter Deposited on Silicon," Journal of Applied Physics, Vol. 53, No. 12, 1982, p. 8988. doi:10.1063/1.330456.

[7] G. H. Haertling, "Ferroelectric Ceramics: History and Technology," Journal of the American Ceramic Society, Vol. 82, No. 4, 1999, pp. 797-818. doi:10.1111/j.1151-2916.1999.tb01840.x

[8] W. Heywang, "Resistivity Anomaly in Doped Barium Titanate," Journal of the American Ceramic Society, Vol. 47, No. 10, 1964, pp. 484-490. doi:10.1111/j.1151-2916.1964.tb13795.

[9] F. Batllo, E. Duverger, J. C. Jules and B. Jonnet, "Dielectric and EPR Studies of Mn-Doped Barium-Titanate," Ferroelectrics, Vol. 109, No. 1, 1990, pp. 113-118.

[10] V. C. S. Prasad and L. G. Kishore, "Studies on Some BaTiO3 Based Commercial Electroceramics," Ferroelectrics, Vol. 120, No. 1, 1990, pp. 141-150. doi:10.1080/00150199008221472.

[11] Y. X u, Ferroelectric materials and their applications, North Holland, New York (1991).