



ISSN: 0975-833X

RESEARCH ARTICLE

SOLID STATE SYNTHESIS OF NIOBIUM AND COBALT DOPED BaTiO₃, XRD, STRUCTURAL AND ENHANCED DIELECTRIC PROPERTIES OF BaTiO₃

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ARTICLE INFO

Article History:

Received 04th July, 2013

Received in revised form

10th August, 2013

Accepted 25th September, 2013

Published online 23rd October, 2013

Key words:

BaTiO₃,
dopants,
Hydraulic Pellet Press,
JEOL 6360A,
HIOKI 3532 LCR HiTester.

ABSTRACT

The synthesis of the doped BaTiO₃ was carried out using the solid state synthesis method. The dopants that used were high purity chemicals of more than 99.9% purity. The dopants used were Niobpentoxide (Nb₂O₅) of Fluka AG and Cobaltous Chloride Hexahydrate (CuCl₂·6H₂O) of Himedia Laboratories. Both the chemicals used were AR grade. The dopants were added as wt% of the basic compound BaTiO₃. The final compound was in powder form. For characterization of the sample it was convenient to use them in the form of pellets using Hydraulic Pellet Press (KP Sr 734) of Himaya Engineers. The powder was inserted in the central hole by weight measurements, of radius 0.5 cm. The powder was inserted and the top punch pressed on the sample. The pressure applied was two tons for a period of two minutes. The process was repeated for all the doped samples. The pellets formed were of one cm in diameter and 4mm thick. The x-ray pattern for all the doped samples were taken and compared with standard reference file. The inter planar distance (d) was calculated and found to be in agreement with the standard reference values confirming the perovskite structure of the Nb and Co doped BaTiO₃. The SEM of the samples was done on JEOL 6360A Analytical Scanning Electron Microscope. The scanning electron image shows distinctly the uniform distribution of the grains. For the various dopant concentrations it is seen that there is change in the grain size. The dielectric properties of the compound sample were measured on HIOKI 3532 LCR HiTester. The instrument provides a wide range of test frequencies from DC and 42 Hz to 5MHz.

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INTRODUCTION

Materials exerting giant dielectric constant have caught the attention of many. Since the discovery of ferroelectricity in a single crystal of Rochelle salt in 1921[1], there have been many attempts to find new materials with greater dielectric constants (k). Due to shortage of mica, the most widely used insulator for capacitors during World War II, there has been an urgent demand for ceramic capacitors with high dielectric constants. This has led to developments in the ceramic capacitor technology. Field of ceramics has been identified as one of the primary fields where improvements in processing and advance products can be anticipated. Most of the industrialized countries in the world have invested heavily in the development of new ceramic materials. This has resulted in production of lower priced ceramic materials with better properties. Due to large variety of chemical, electrical, biological and mechanical properties that the ceramic materials exhibit, there is no social and industrial application without ceramics.

Ceramics are different from glasses and single crystals as they are composed of and aggregate of randomly oriented crystallites intimately bonded to form a solid structure. Although crystallites possess an ordered internal structure like a crystal ceramics have isotropic character and are polycrystalline materials. The area of interest of present study is Electro ceramics which are highly specialized class of materials. Their properties are predominantly controlled by their composition in addition to processing conditions and their complexities of shape. Various types of Electro ceramics are insulators, Ferrites, capacitors, PTC materials, ferroelectrics, piezoelectric, pyroelectrics, electro-optic materials etc [2]. The material which possess the spontaneous polarization even in the absence of electric field and the direction of spontaneous polarization can be changed by applying and electric field are called ferroelectric materials and the phenomenon is called Ferroelectricity [3]. Barium Titanate is a ferroelectric material which is widely used in electronic industry for various application such a capacitors, PTCR and transducers. The material exists in four crystal structures viz. Cubic, Tetragonal, Orthorhombic and rhombohedral. There are large variations in permittivity and dielectric loss associated with structural phase transitions. To eliminate such disadvantages doping is

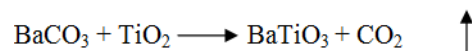
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employed for materials in electronic devices. The dielectric constant has to be controlled within 15% of the dielectric constant at room temperature. Niobium (Nb) and Cobalt (Co) are added to stabilize permittivity and reduce dielectric loss [4-5].

Experimental technique:

The starting material for the synthesis was 99.9% pure BaCO₃ and TiO₂. The two powders were mixed in the required stoichiometric ratios. The powders were thoroughly milled with mortar and pestle. The milling operation was carried for more than four hours. After milling the powder was calcinated at 1100°C for four hours in silica crucible in muffle furnace. The reaction for the formation of BaTiO₃ is as follows



The final weight of BaTiO₃ was taken to be 21.20 gms, which was 1/11 its molar weight. The dopants were added as wt% of this weight of BaTiO₃.

Synthesis of Niobium and Cobalt doped BaTiO₃

The synthesis of the doped BaTiO₃ was carried out using the solid state synthesis method. The dopants that used were high purity chemicals of more than 99.9% purity. The dopants used were Niobpentoxide (Nb₂O₅) of Fluka AG and Cobaltous Chloride Hexahydrate (CuCl₂·6H₂O) of Himedia Laboratories. Both the chemicals used were AR grade. The dopants were added as wt% of the basic compound BaTiO₃. The following table shows the sample name with their doping concentration.

BaTiO ₃	Dopants (Nb ₂ O ₅ + CuCl ₂ ·6H ₂ O)				
Sample No.	SO1	SO2	SO3	SO4	SO5
Weight of	0.025%	0.05%	0.1%	0.2%	0.4%
21.20 gm	dopants in mg	5.3	10.6	21.2	42.2
	(each) as wt%				84.8
	of BaTiO ₃				

The following table gives the composition of the dopants in atomic % (at %). The table also gives the Nb + Co along with the Nb/Co ratio.

Sample	Nb ₂ O ₅	CoCl ₂	Nb + Co	Nb/Co
SO5	0.35	0.72	1.07	0.486
SO4	0.18	0.36	0.54	0.5
SO3	0.09	0.18	0.27	0.5
SO2	0.04	0.09	0.13	0.44
SO1	0.02	0.04	0.06	0.5

The compound after the addition of the dopants was milled using mortar and pestle for more than 3 hours each. To get good homogeneity the final compound was calcined in silica crucible in muffle furnace for four hours continuously at 1100°C. The compound after calcinations was allowed to cool naturally.

Pelletization and Firing

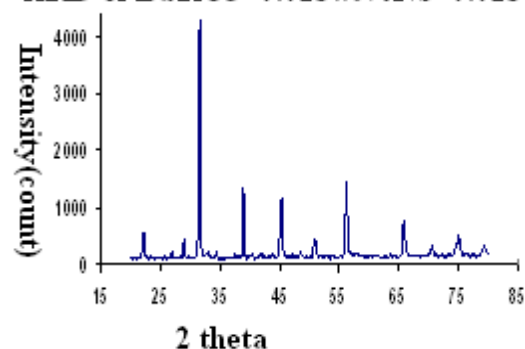
The final compound was in powder form. For characterization of the sample it was convenient to use them in the form of

pellets. The pellets should be of the same physical dimensions. Initial pellet making failed because of the pellet was not able to maintain its form. As a result binder was added to the compound for providing binding force in the formation of pellets. The binder was Polyvinyl Alcohol (PVA) and was added as few drops to each of the sample. Pellets were formed using Hydraulic Pellet Press (KP Sr 734) of Himaya Engineers. The powder was inserted in the central hole by weight measurements, of radius 0.5 cm. The powder was inserted and the top punch pressed on the sample. The pressure applied was two tons for a period of two minutes. The process was repeated for all the doped samples. The pellets formed were of one cm in diameter and 4mm thick. The pellets were hard enough for characterization and were ready for firing.

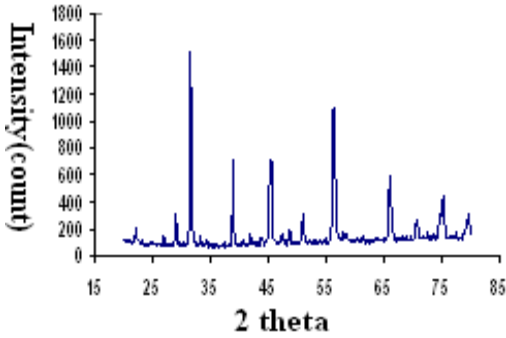
Firing is a process of giving heat treatment to the product to get better bonding amongst the particles of the compound [6]. Better bonding is necessary to obtain the desired properties and the structure. The temperature for firing is such that there is no phase transition but to remove the organic additives that were used as binder and other byproduct gasses. The pellets were placed in a silicon boat and fired in the muffle furnace up to 1200°C for four hours. The PVA decomposes at 400°C [7]. After heating the pellets were allowed to cool naturally. The pellets were finally ready for characterization. The diameter, thickness of the pellets was measured using vernier calipers. The x-ray powder diffraction method was performed on Bruker AXS, D-8 Advance X-ray Diffractometer, with the range of Bragg angle from 20° to 80° in steps of 0.1°. The rays were Cu K rays with wavelength of 1.5419 units. The x-ray pattern for all the doped samples were taken and compared with standard reference file. The inter planar distance (d) was calculated and found to be in agreement with the standard reference values confirming the perovskite structure of the Nb and Co doped BaTiO₃. The structure was orthogonal perovskite structure. The experimental vales of the inter planar distance (d) in units is tabulated as

hkl	Standard Reference data	Experimental data
	d (Å)	d (Å)
011	0.062	0.062
101	0.094	0.092
022	0.248	0.249
111	0.125	0.125
222	0.500	0.498
102	0.1866	0.1867
211	0.315	0.312
131	0.3738	0.3742
311	0.6301	0.6250
213	0.5615	0.5599

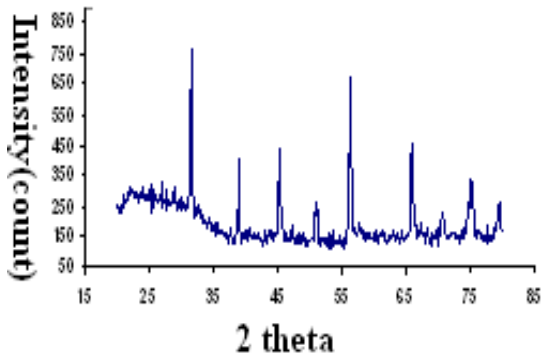
XRD of BaTiO₃+0.025wt%Nb+0.025wt%Co



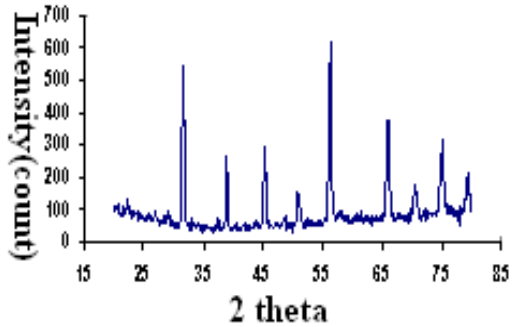
XRD of BaTiO₃+0.05wt%Nb+0.05wt%Co



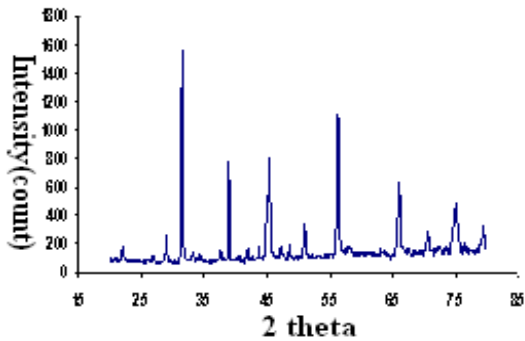
XRD of BaTiO₃+0.1wt%Nb+0.1wt%Co



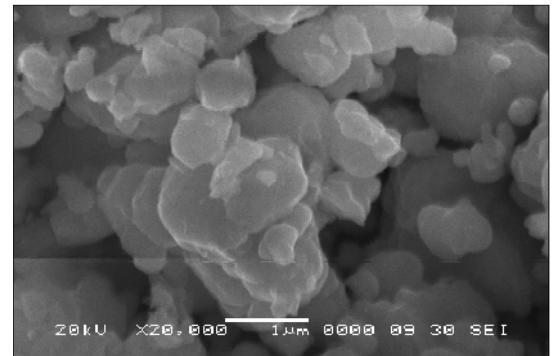
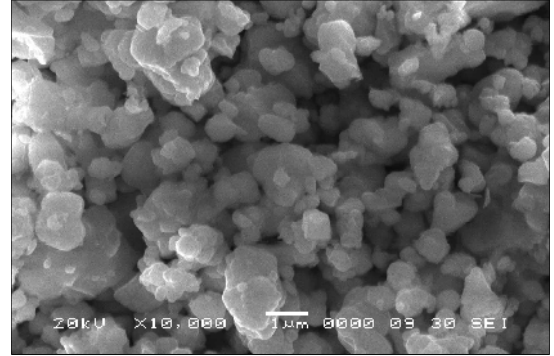
XRD of BaTiO₃+0.2wt%Nb+0.2wt%Co



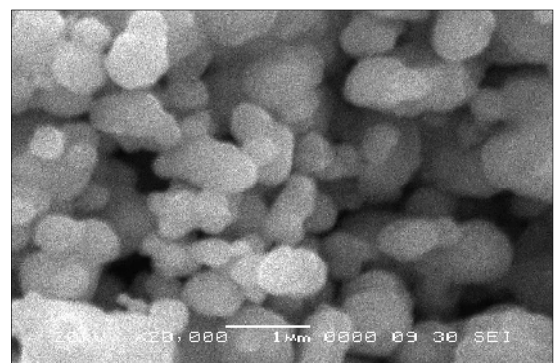
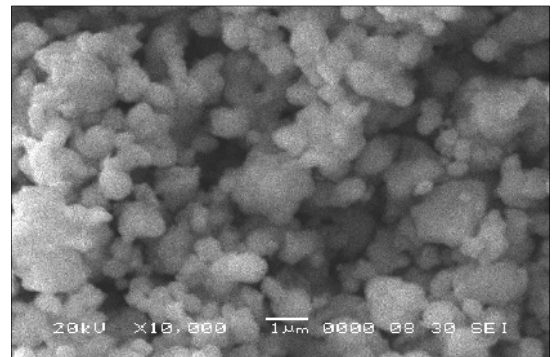
XRD of BaTiO₃+0.4wt%Nb+0.4wt%Co



0.4wt% doping. At 0.4wt% and above doping there is influence of Nb on the grain structure [9]. It can thus be concluded that the orthorhombic structure is maintained and higher doping concentration of Nb influences are seen in this phase. The SEM of the samples was done on JEOL 6360A Analytical Scanning Electron Microscope. The images are as shown from Fig. 4.2 – 4.6 for differently doped BaTiO₃ compound.

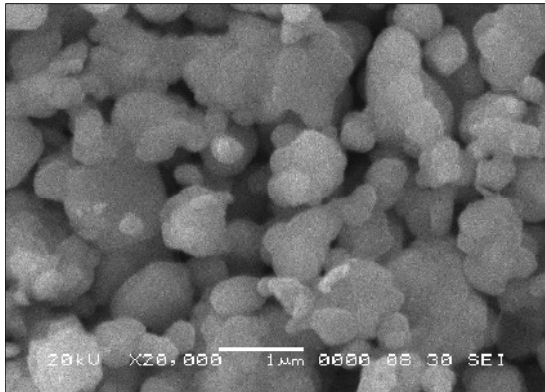
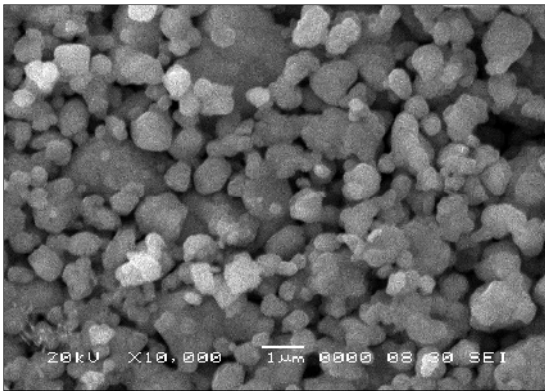


BaTiO₃ doped with 0.025wt% Nb and 0.025wt% Co.

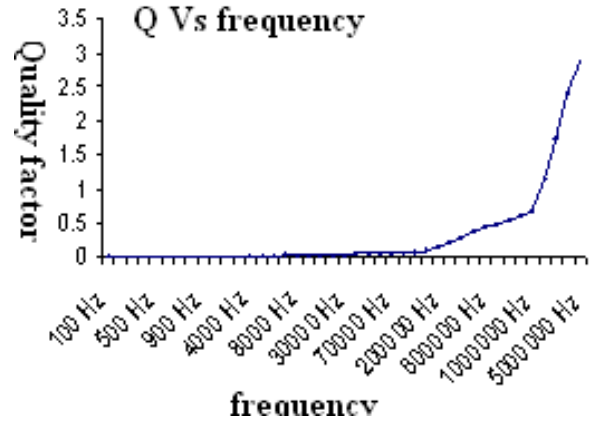
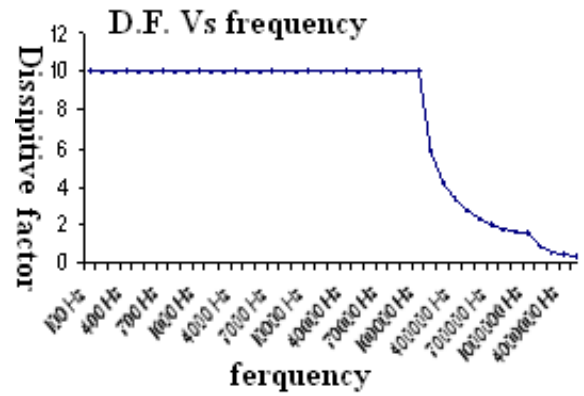


BaTiO₃ doped with 0.05wt% Nb and 0.05wt% Co.

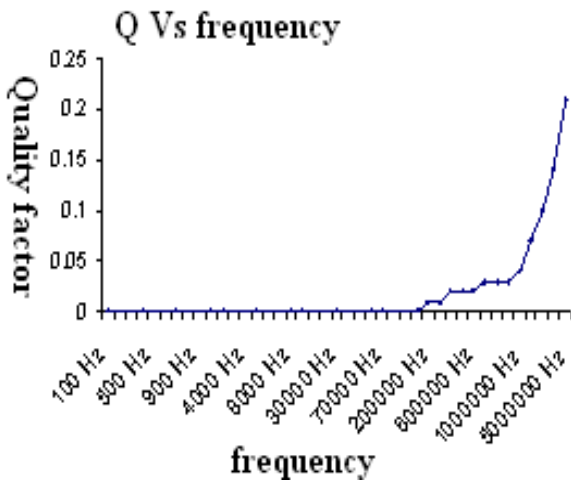
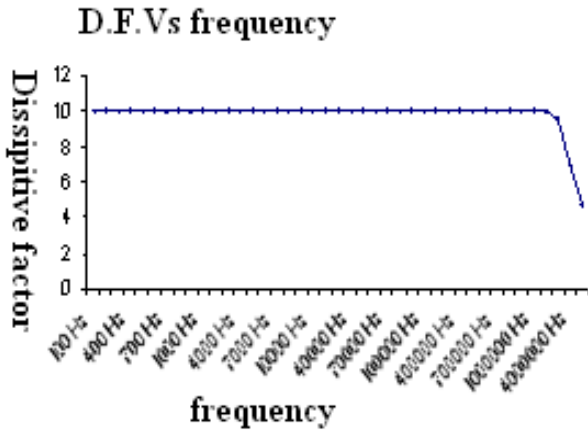
The x-ray analysis of the powder showed that the structure of the Nb and Co doped BaTiO₃ was orthorhombic with the values of the lattice parameters $a = 3.980$, $b = 5.671$ and $c = 5.690$. The values of the lattice parameters were in agreement with the standard values. The Nb dopants influence in the orthorhombic phase and the Co dopant influences in the tetragonal phase [8]. The plots also show the decrease in intensity up to 0.2wt% doping with a rise in the intensity in



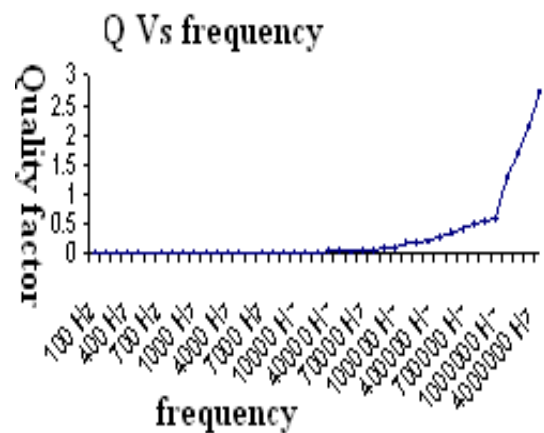
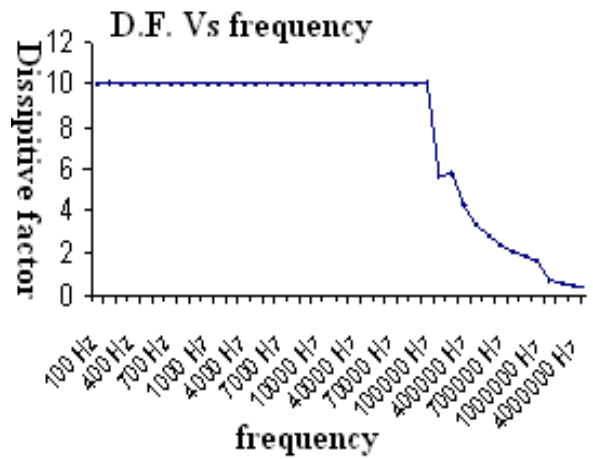
BaTiO₃ doped with 0.1wt% Nb and 0.1wt% Co.



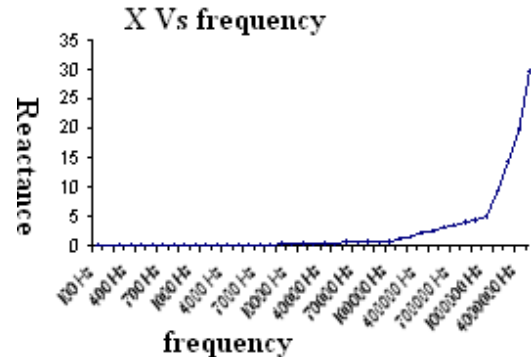
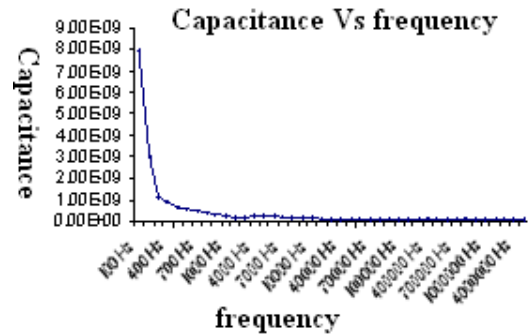
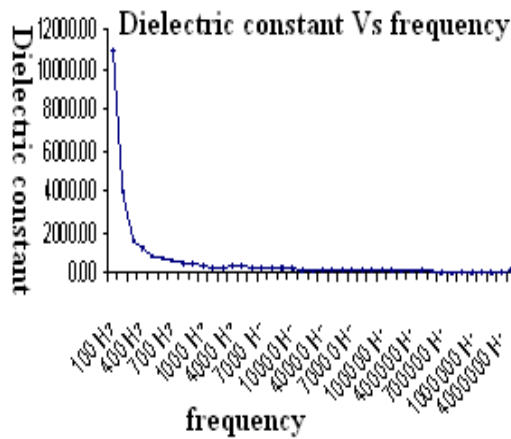
BaTiO₃ doped with 0.05wt% Nb and 0.05wt% Co.



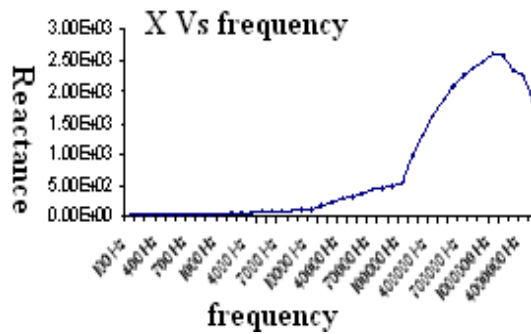
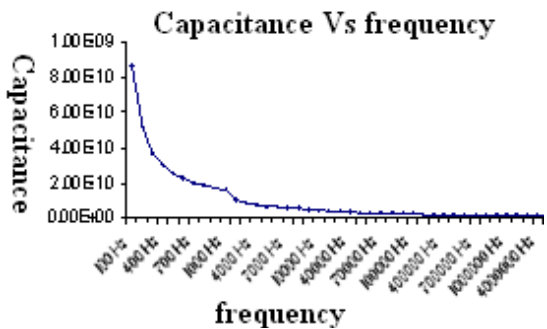
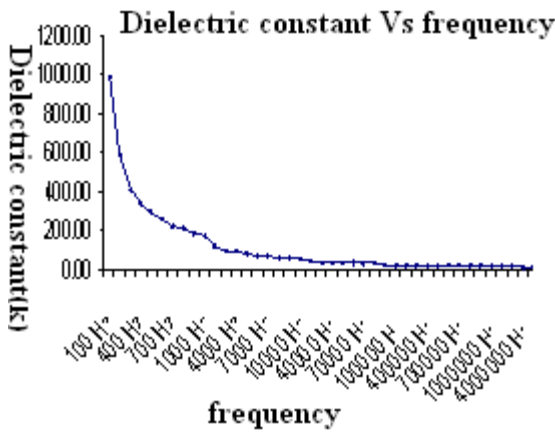
BaTiO₃ doped with 0.025wt% Nb and 0.025wt% Co.



BaTiO₃ doped with 0.1wt% Nb and 0.1wt% Co.

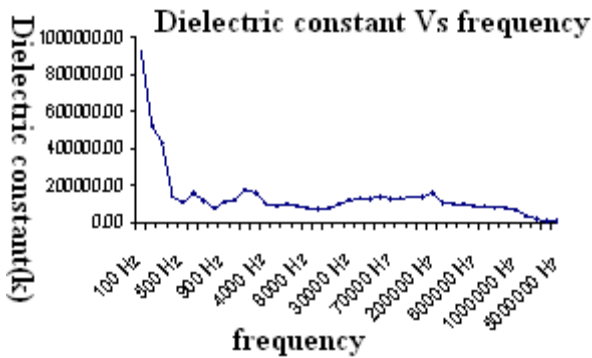


BaTiO₃ doped with 0.025wt% Nb and 0.025wt% Co.



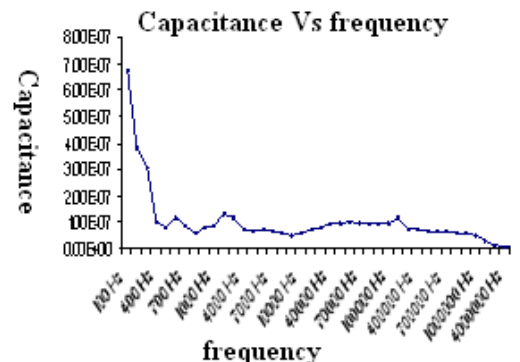
BaTiO₃ doped with 0.05wt% Nb and 0.05wt% Co.

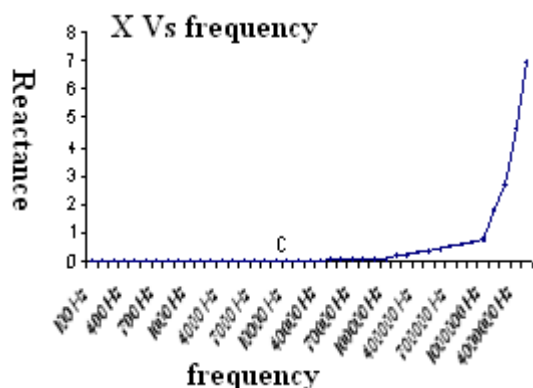
BaTiO₃ doped with 0.025wt% Nb and 0.025wt% Co. BaTiO₃ doped with 0.05wt% Nb and 0.05wt% Co.



BaTiO₃ doped with 0.1wt% Nb and 0.1wt% Co.

The scanning electron image shows distinctly the uniform distribution of the grains. For the various dopant concentrations it is seen that there is change in the grain size. The grain size was calculated using Contrell method [10]. The method gives the relation between the number of intercepts and the grain boundary per unit length of reference circle [11]. The dielectric behaviour of the compound is interpreted from the graphs. give the variation of Dissipation factor (DF) and quality factor (Q) with frequenc. One more interesting observation was the behaviour of the value of the Capacitance and Reactance with frequency. As expected, the nature of variation of Capacitance and Reactance with frequency was in tune with the other observed variations viz. DF and quality factor. The graphs of Capacitance and Reactance with frequency are as shown.



BaTiO₃ doped with 0.1wt% Nb and 0.1wt% Co.

RESULT AND DISCUSSION

Ceramic materials and single crystal exhibiting ferroelectric properties are extensively used in electronics and optics. Ferroelectricity is an interdisciplinary field of research having extensive applications in the field of engineering and technology [12]. BaTiO₃ material exhibits good dielectric properties. The X-ray data gave the lattice parameters of the doped sample which were in excellent agreement with reported data [13 - 15]. The frequency characteristics of different parameters viz. dielectric constant, quality factor, reactance etc of the samples were studied.

Conclusion

The properties of ferroelectric materials change drastically in the vicinity of Curie temperature and phase transition temperature. The present work has been an effort in understanding the basic physical properties and the effect of Nb and Co additives in BaTiO₃. The structure of BaTiO₃NbCo estimated to be orthorhombic. Some of the peaks of the X-ray data remained unknown. The interplanar distance "d" gave the lattice parameters $a = 3.98$, $b = 5.671$ and $c = 5.689$

which were in good agreement with reported data. The grain size found for 0.1wt%, 0.2wt% and 0.4wt% samples are in agreement with those found for Nb rich specimen [16]. The response of the dielectric constant, Dissipation factor, Quality factor for a wide range [100Hz – 100 kHz] of frequency was flat.

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