Synthesis and Structural Study of Cr-Doped $BaTiO_3$ by X-ray Diffraction Technique and Williamson-Hall and Size Strain Plot Methods

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Abstract.X-ray diffraction technique has been employed in the current research work to determine the structure and composition of Cr-doped $BaTiO_3$, because it is a very useful tool to study non-destructively the crystallographic structure, chemical composition and physical properties of $BaTiO_3$. The XRD characterization has been conducted at IUC, UGC-DAE CSR. The synthesis of the nano-material has been done using the Sol-Gel Auto Combustion technique. $BaTiO_3$ is a versatile compound, predominantly known for its storage capacity. Thus, serving in innumerable devices such as MLCCs, PTCR and microwave dielectric ceramics. Analysis of the obtained data from the characterization techniques has been done using Origin software. The powder XRD confirms the crystalline compound of Cr-Doped $BaTiO_3$ by comparing 2θ and intensity values with JCPDS values of the same compound.

INTRODUCTION

Barium Titanate is a ferroelectric ceramic which is extensively used for the manufacture of humongous kind of electro-ceramics owing to the fact that barium titanate has excellent dielectric and piezoelectric properties. Because of its versatile properties, it has become very interesting to study such type of compounds. The current research work is mainly focused on it[1]. Literature surveysuggests that, XRD is the best tool to probe the crystallographic structure of such type of materials.These are therefore used in application of various components such as multilayer capacitors, thermistors, gas sensors, dynamic random access memory (DRAMs), optical devices, infrared detectors, transducers, etc. In general, they work at room temperature. So, the T_c(Curie temperature) of the ferroelectric materials($BaTiO_3$) should also be at room temperature.It is widely known that T_c of $BaTiO_3$ is about 1200°C, but it can be modified to achieve a particular application by varying the composition and thereby changing its ceramic microstructure, or doping, which substitutes either into Barium or on the Titanium sites or both. One can dope a variety of element for the modification of $BaTiO_3$ or any other ferroelectric materials for fetching various applications from finally prepared material. Many experiments tend to study the Positive Temperature Coefficient of Resistivity (PTCR) behavior of modified $BaTiO_3$[2]. Many researchers are working on the pyro-electric properties of ferroelectric materials for the application of infrared detectors because of high response in the infrared wavelength range and their ability to operate at room temperature without expensive cooling systems.

EXPERIMENTAL DETAILS

Polycrystalline BTO and Cr^{3+} doped BTO i.e., $BaTi_{0.95}Cr_{0.05}O_3$ (BTCO) were prepared using Titanium (IV) butoxide, reagent grade, 97%, Barium Nitrate 98.5%, extra pure ($Ba(NO_3)_2$), Chromium (III) nitrate (nonahydrate) 97.0% ($Cr(NO_3)_3.9H_2O$) powders. The components were weighed as per stoichiometric ratios and BTO was synthesized using sol-gel auto combustion method[3]. The obtained xerogel was then calcined for 2hrs (2 hrs. of reaching time and 2 hrs. of stable calcination) in alumina crucible. The calcined material (the final product) was

then, grinded for 30 minutes. The X-ray diffraction patterns of the sample were recorded at room temperature. The BTO sample was identified as tetragonal phase (JCPDS file #:89-1428). On comparison with, lattice parameters of Barium titanate (i.e., BTO) {a=0.0045, c=0.0420} with that of Cr-doped $BaTiO_3$ (i.e., BTCO) the lattice parameters that were obtained are shown in table.

RESULTS AND DISCUSSION

1. XRD analysis: X-ray diffraction (XRD) is a very important and powerful method for the study of nano-materials for it helps one to probe the structure of the material under consideration (with the restriction that at least one of the material's dimensions should be in the range of 1-100nm)[4]. It allows one to measure the atomic spacing, the miller indices, crystallite size, volume, density, phase composition; lattice strain and crystallographic orientation andall of these parameters cover more or less everything that one needs to probe the structure of a bulk material. A.W. Hull in 1919 gave a paper, where he quoted that, "Every crystalline substance gives a pattern; the same substance always gives the same pattern; and in a mixture of substances each produces its pattern independently of the others. The X-ray diffraction pattern of a pure substance is, therefore, like a fingerprint of the substance." This is the sole reason why powder diffraction method is ideal for characterization and identification of polycrystalline phases. XRD technique is a very useful characterization tool to study, non-destructively the crystallographic structure, chemical composition and physical properties of $BaTiO_3$.Bruker D8 Advance XRD was installed in June 2010. This diffractometer is equipped with a sealed Cu-Kα X-ray source.

In the present study, the XRD data for 5% doping of Chromium fetches the graph with distinct peaks as shown in fig: 1(a) which is quite similar to the standard BTCO peaks as can be seen in the JCPDS file. Similarly, the graph for 10% and 15% doping can be seen in fig: 1(b) and fig: 1(c) respectively.

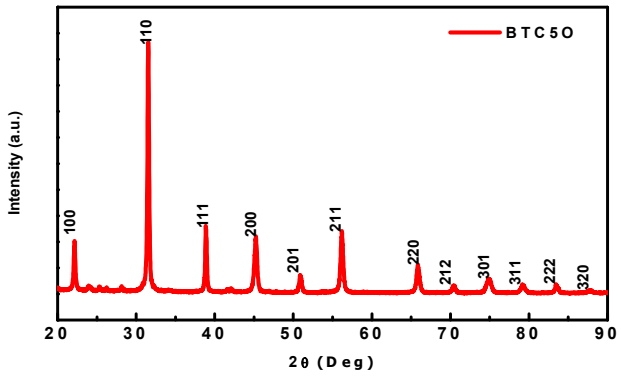

FIGURE 1(a). X-ray Diffraction graph of Chromium doped $BaTiO_3$ (5% doping)

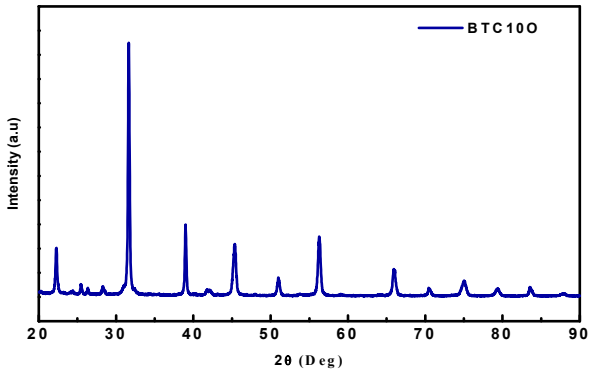

FIGURE 1(b). X-ray Diffraction graph of Chromium doped $BaTiO_3$ (10% doping)

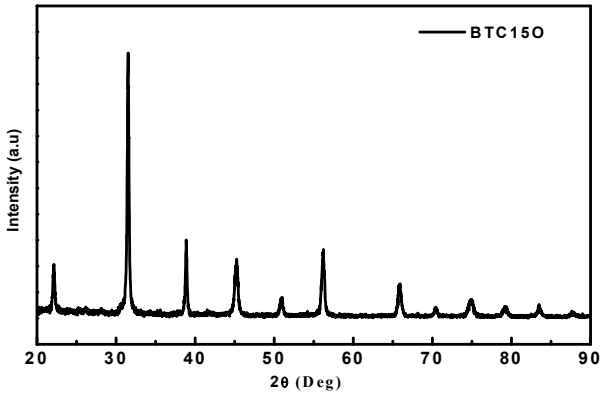

FIGURE 1(c). X-ray Diffraction graph of Chromium doped $BaTiO_3$ (15% doping)

In the present research paper the author have used Debye Scherrer's method for calculation of the crystallite sizewhich is stated as below:

$$D = \frac{K\lambda}{(\beta 2_{measured} - \beta 2_{instrumental})\cos\theta}$$

Here, k is the shape factor (~0.8-1.39), D is the mean size of the crystallite thickness, λ =0.154 nm, θ is the Bragg angle, and β is the full-width at half-maximum (FWHM) of the peak (radians) corrected for instrumental broadening. $\beta_{measured}$ and $\beta_{instrumental}$ are the FWHMs of the sample and a standard, respectively. The standard is typically a highly crystalline sample with a diffraction peak in a similar position to the sample. The peak width gives the thickness of the crystallites perpendicular to those planes.

2. Williamson-Hall Plot: This method is attributed to G.K.Williamson and his student, W.H.Hall. It is based on the principle that the approximate formulae for size broadening, β_L, and strain broadening, β_e, vary quite differently with respect to Bragg angle, θ:

$$\beta_{tot}\cos\theta = \mathbf{C}\varepsilon\sin\theta + \frac{K\lambda}{L}$$

The above equation describes the uniform deformation model[5], where the strain is assumed to be the same in all the crystallographic directions. Here, the graph has been plotted between "βcosθ" and "4sinθ". In fig 2(a),fig 2(b), and fig 2(c) the particle size is determined by the slope of the linearly fitted data and strain[7] by y-intercept of the graph and the corresponding results are reported in Table 2.

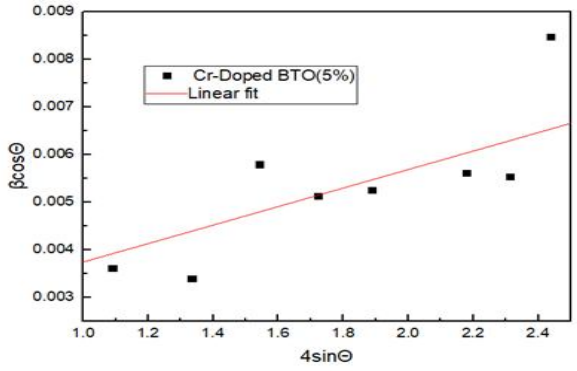

FIGURE 2(a). The W-H analysis of Cr-doped $BaTiO_3$ (5%) calcinated at 900°. The strain is extracted from the slope and the crystalline size is extracted from the y-intercept of the fit

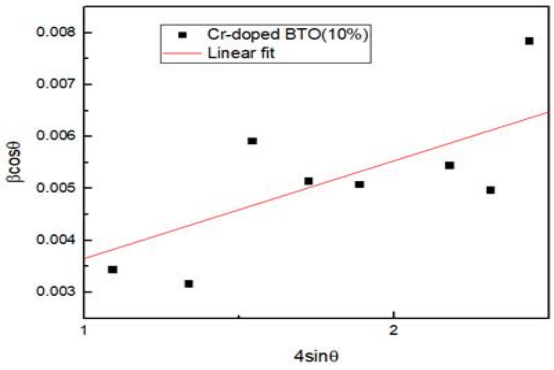

FIGURE 2(b). The W-H analysis of Cr-doped $BaTiO_3$ (10%) calcinated at 900°. The strain is extracted from the slope and the crystalline size is extracted from the y-intercept of the fit.

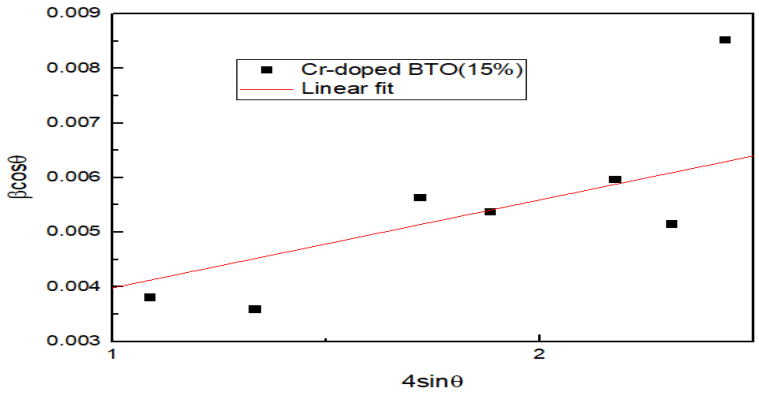

FIGURE 2(c). The W-H analysis of Cr-doped $BaTiO_3$ (15%) calcinated at 900°. The strain is extracted from the slope and the crystalline size is extracted from the y-intercept of the fit.

TABLE 2: XRD Parameters

Parameter	5%	10%	15%
Crystallite size (Debye Scherrer)	32.6048 nm	33.7048 nm	29.6439 nm
Crystallite size (Williamson Hall Plot)	77.4301 nm	78.3051 nm	58.4810 nm
Lattice parameters(a ,c)	(3.9954, 3.9975)	(3.9996, 3.9876)	(4.0053,4.0122)
Strain (using Williamson Hall Plot)	$1.95 \times 10^{-3} \pm 0.00004$	$1.88 \times 10^{-3} \pm 0.00004$	$1.61 \times 10^{-3} \pm 0.00005$
Volume(a^2c)	63.8129	63.7888	64.3654
Volume (Rietveld)	64.532	64.049	64.4105
Intercept	$0.00179 \pm 9.21054 \times 10^{-4}$	$.00177 \pm 0.001$	0.00237 ± 0.00106
Strain	1.95×10^{-3}	1.88×10^{-3}	1.61×10^{-3}

CONCLUSION

The intensity versus 2θ graph represents the XRD pattern of the synthesized material. This can be seen in fig 1(a), fig 1(b), and fig 1(c). Distinct planes are designated with the corresponding hkl plane names, which is quite evident in the graphs.Similarly, the Williamson-Hall plot between various doping concentrations (here, 5%,10% and 15%) can be seen in fig:2(a), fig 2(b) and fig 2(c). This figure gives the corresponding values of the intercept and the slope (the value of which can further be utilized to obtain the strain values).

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