Synthesis, structural & dielectric properties of Cr doped $Ba_5Ti_2O_7Cl_4$ single crystal

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Abstract: Single-crystal of Cr-doped ferroelectric $Ba_5Ti_2O_7Cl_4$ was synthesized with BaCl2 as a flux by a high temperature solution growth technique. X-ray diffraction studies of the crystal refers to a single phase with an orthorhombic structure. All the parameters of dielectric properties were studied with varying temperature describe the electronic behavior of doped $Ba_5Ti_2O_7Cl_4$, single crystal which was confirmed by thermal analysis of the DTA curve. The measured loss tangent of the crystal, which is in good agreement with the dielectric studies. The ferroelectric property of the crystal was confirmed by studying the hysteresis loop. In this study, several parameters, like the coercive field and spontaneous polarization, were measured and calculated.

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1 Introduction

Ferroelectric material has a variety of applications in today's era and have been used formation of thin films, single crystals, and bulk ceramics for different applications [1] piezoelectric and pyroelectric applications, miniature capacitors. They are used in making nonvolatile memories, electro-optic switches, dynamic random-access memories, optic modulation, capacitor, waveguide and many more[2-5]. Growing a single crystal is important for studying the optical, nonlinear optical, and dielectric properties of the single crystal; for this reason, various techniques have been applied to get large, high-quality single crystals [6]. Barium Titanium oxide Barium hypochloride, lead-free ferroelectric material was synthesized by using flux methods at 1260^{o}C in the efforts to grow pervoskite and related materials [7, 8]. The properties of pervoskites such as pyroelectricity, piezoelectricity, dielectric susceptibility,, etc are of gross effects and vary enormously from one pervoskite to another and differences in crystal structure are hardly apparent. Recently, however, the BaTio3 and related materials crystal have been a focus of growing interest for ferroelectric applications due to its peculiar properties, including the occurrence of phase transitions, a high dielectric constant, the formation of a hysteresis loop, and the formation of domains [9]. In the past decade, domain engineering, which is mainly based on ferroelectrics, has attracted considerable attention and has been widely studied [10]. The changes in physical properties of ferroelectric or

pervoskites are also remarkable when introduced to doping. Generally, doping could be in the bismuth oxide layer or in perovskite-like units (A or B sites) [11]. Millan et al. reported the substitution of Pb2+ in (Bi2O3) 2+ layers by other cations, such as Sb3+, Sn2+ or Te4+, within the perovskite-like units; partial substitution of strontium ions by bismuth ions increased the Curie tem-perature and improve the dielectric properties of ferroelectric [12].

In a present study the lead free complex pervoskite, single crystals are very promising materials for electronic devices and applications such as capacitors, actuators, sensors, transducers [13]. Therefore, it is of special interest due to very large electro-optic properties and good dielectric properties [14]. These properties have been studied by using chromium impurity [15]. As the role of impurities in ferroelectric crystals is increasingly being realized, they affect the vital parameter like domain structure and phase transition temperature, of particular importance that impurities can convert non ferroelectric crystal in to ferroelectric under suitable condition [10]. It is thus obvious that these impurities develop a strong large distance cooperative interaction in the structure. In this article, we attempt to investigate the effect of chromium impurity on perovskite $Ba_5Ti_2O_7Cl_4$ structure, dielectric, ferroelectric properties.

2 Experimental studies

In this laboratory, Ingle et al. [7, 16] grows a pure $Ba_5Ti_2O_7Cl_4$-single crystal by using flux method and carried out a detailed study about the structural, dielectric and domain properties of undoped $Ba_5Ti_2O_7Cl_4$-single crystals using characterizations technique use has limitations. Recently, this laboratory has extended this study by growing doped $Ba_5Ti_2O_7Cl_4$-single crystal with Cr_2O_3.

2.1Growth of $Ba_5Ti_2O_7Cl_4$ single crystal

The single crystals of $Ba_5Ti_2O_7Cl_4$ were grown by taking mixture of $BaCl_2$, $BaCO_3$ and TiO_2 in the molar ratio of 1:1.5:1 respectively so as to form a mass of 30 gm. The dopant Cr_2O_3 (0.017% 5 mg) added to this mixture respectively. This mixture was dried at 200ºC for twohours to remove moisture and then grounded together in the mortar for 6 h. these mixtures were placed in a 50 ml platinum crucible covered with a platinum lid and introduced to furnace at 1250ºC. The rate of heating was 100ºC/hr from room temperature to 600ºC; 80ºC/hr from 600ºC to 1000ºC and 25ºC/hr from 1000ºC to 1250ºC. The crucible maintained at this temperature for 5 hrs to give soaking time. The homogeneous mixture then cooled to 900 °C at the rate of 25 °C/hr to allow for crystallization. The material was reheated, to 1250 °C, and slowly cooled to room temperature at the rate of 25 °C/hr for the complete crystal growth [13].

2.2 Crystal structure determination and dielectric studies

An X-ray powder diffraction pattern were recorded for the crystal using X-ray diffractometer with monochromatic Cu Kα radiation at glancing angles 2θ range 3°–90°. Thermoanalytical studies like DSC, TGA, DTA were carriied out to study the phase transitions, changes occuring with temperature.LCR Tester (Gwinstek–Make, High precession LCR Meter, Model No. 821, Frequency range 12 Hz to 200 kHz) is used to measure the dielectric constant (εr), and dielectric loss (tan∂) at the desired frequencies with varying temperature range. It gets the dielectric constant peak nearby phase transition temperature and this study the shows contribution of different polarization towards the dielectric property of the material at different temperatures and frequencies. The material nature is found to be relaxor or normal ferroelectric which can also be

detected by studying at different frequencies. The sample coated with a silver paste to have coductivity for the dielectric measurement. The measurements recorded from room temperature to 960 °C at different frequencies. It interfaced the LCR meter with the computer and the data (capacitance and D factor) collected as a function of temperature [9].

2.3 Hysteresis loop studies

The ferroelectric hysteresis loop is observed using the TFAnalyzer testing system at IIT, Mumbai. This study used for the measurement, of a various parameter of ferroelectric hysteresis loop such as spontaneous polarization (Ps), remanent polarization (Pr), coercive field (Ec) [17].

3 Result and discussion

3.1 Structural properties

Fig 1 shows the XRD patterns of the $Ba_5Ti_2O_7Cl_4$ single crystal, reveals also very well convergence to the standard pattern[17]. It is seen that the entire composition owns a single phase perovskite structure, and it detects no trace of any secondary phase [18, 19]. show A better homogeneity and crystallization of the samples is justified by sharp and single diffraction peaks [20, 21]. Other peaks of the plot indicate phase transition and crystalline nature of the sample. The diffraction lines peaks are indexed in different crystal systems, unit cell configurations and the Powder- X program is used to calculate lattice parameters of $Ba_5Ti_2O_7Cl_4$ single crystal. It is observed that pure and Cr3+ doped $Ba_5Ti_2O_7Cl_4$ belong to the orthorhombic structure[7, 8]. The shifting orthorhombic state of the line towards low angles is highly sensitive to the little change of compositions [22]. Therefore, orthorhombic changes and give rise to tetragonal and tetragonal change and give rise to orthorhombic [23, 24, 25]. Thermal analysis also explains this phase transitions. A good agreement between The calculated and observed d-values of all diffraction lines (Reflection) of $Ba_5Ti_2O_7Cl_4$ single crystal are in fine agreement X-ray pattern, with the different compositions, suggests that there is no change in the basic crystal structure of $Ba_5Ti_2O_7Cl_4$ single crystal [7, 26]. The values of lattice parameters of Cr doped $Ba_5Ti_2O_7Cl_4$ single crystal match with that of pure $Ba_5Ti_2O_7Cl_4$ single crystal[8]. Thermo analytical methods involve the measurements of various properties of materials subjected to dynamically changing environments under predetermined condition of heating rates, temperature range,etc [27-29]. Thermal analysis is carried out in the powder sample in a temperature ranging from room temperature to 1200 °C with a heating rate of 10 °C/min. Figure 2 & 3 shows TGA & DTA curve respectively for Cr doped $Ba_5Ti_2O_7Cl_4$ single crystal. It observes two small endothermic peaks at 80 °C and 890 °C. These peaks correspond to the phase transitions as it observes the peaks without loss of mass [30].

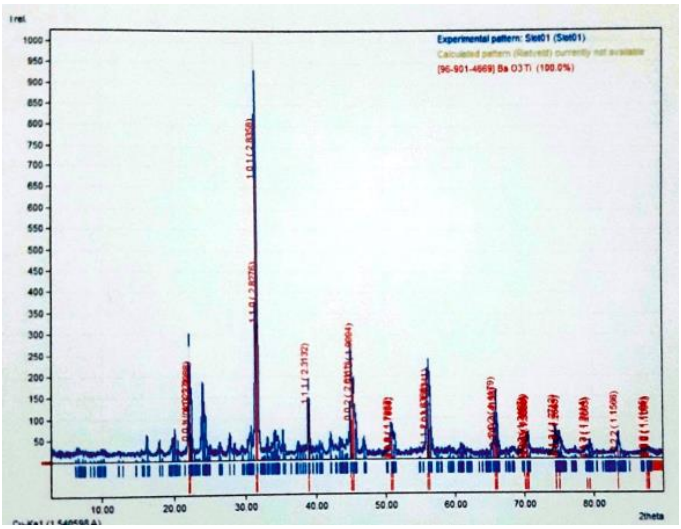

Fig. 1 X-ray diffraction pattern of Cr doped $Ba_5Ti_2O_7Cl_4$

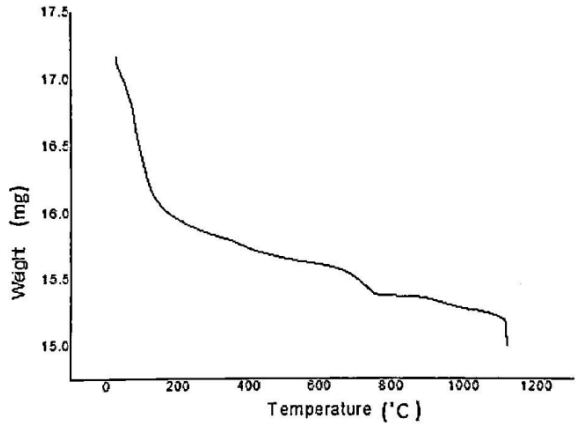

Fig2TGA thermo-gram for Cr doped $Ba_5Ti_2O_7Cl_4$

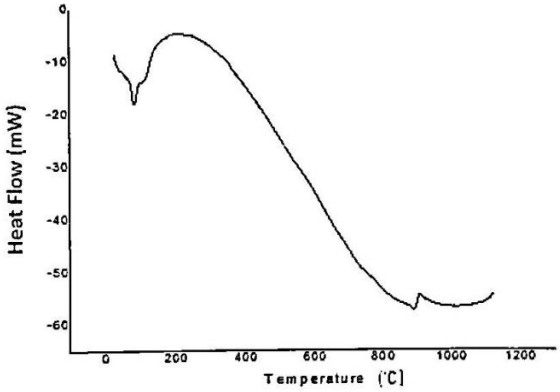

Fig3DTA thermo-gram for Cr doped $Ba_5Ti_2O_7Cl_4$

3.2 Dielectric properties

Fig. 4 shows the variation of dielectric constant with respect to a temperature at different frequencies of Cr doped $Ba_5Ti_2O_7Cl_4$. At room temperature dielectric constant is 5.181×10^3 it drops to 2.573×10^3 at 80°C and rises to 4.6×10^9 at 910°C corresponding to phase transition and Curie temperature respectively. The dielectric constant at room temperature for 1 kHz is very low as compared to 100 Hz i. e. 1.69 X 10^2 at 80°C, it starts increasing and becomes highest i.e. 7.91 X 10^7 at 920°C. The dielectric constant is also affected by the frequency of the applied electric field or the frequency of other electromagnetic fields impinging on the material. The measurement of the dielectric constant on the small samples formed by cutting shows that the dielectric constant at room temperature was of the specific order[17]. A little variation in dielectric constant values is observed from sample to sample at room temperature. However, in every case it is found that there is rise up to the Curie temperature, the dielectric constant value increases with increasing

temperature, and decreases with changing frequency (spurt) at the Curie temperature [31]. It is found that the Curie temperature [32] is about 910 °C and depends upon impurity level in the crystal. The dielectric constant at this temperature lies in the range of 10^8 to 10^9 which shows that the crystal belongs to the category of induced dipole type ferroelectrics [33]. Figure 5 show the variation of loss tangent with a temperature at different frequencies. The inverse of loss tangent, Q found to reduce at greater value of frequency which indicates suitability of material at higher frequencies. [19]. The loss factor is comparatively small at lower electric fields, but increased doping it becomes prominent at higher field values. Loss tangent tan ɗ is important because all these ferroelectric materials have a higher dielectric constant than other materials. It make these ferroelectric materials useful for miniaturization; the resultantly capacitor becomes thin and tiny. With an increasing dielectric constant, loss tangent also increases. Therefore, the dielectric constant is directly proportional to the loss tangent [34]. It happens because of thermal agitation. Thus, the miniaturization of a capacitor happens because of property. In this study, the most probable cause of high dielectric loss is because of an increase of leakage current depending on the crystal structural impurities, like vacancies, dislocation, or ionic charge balance [35, 36].

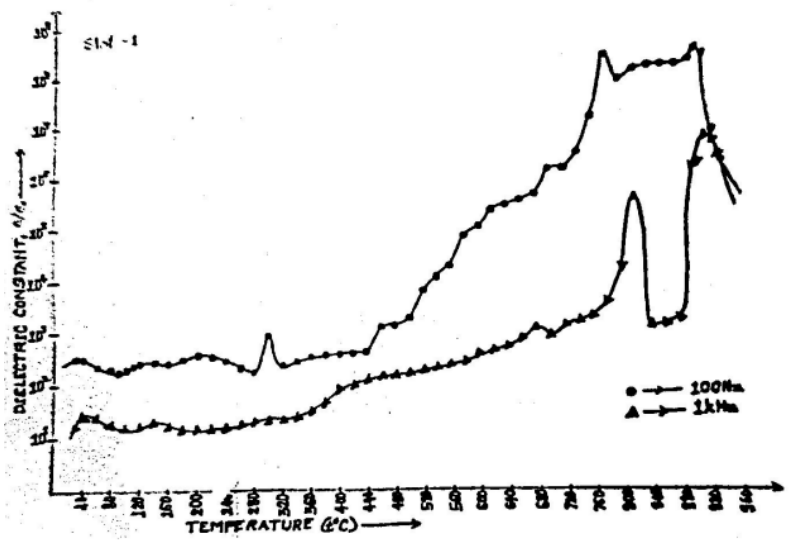

Fig 4 Temperature dependent dielectric constant of doped $Ba_5Ti_2O_7Cl_4$ at 100 Hz & 1 kHz

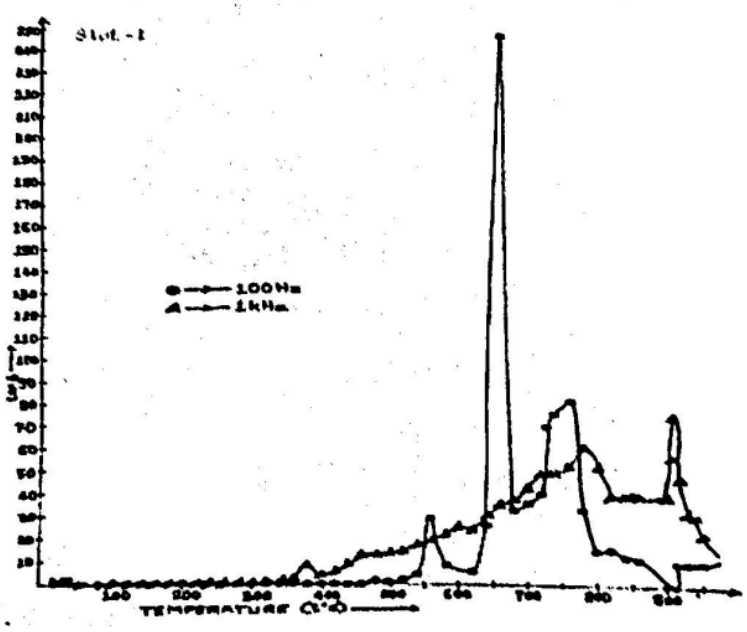

Fig 5 Temperature dependent dielectric loss of doped $Ba_5Ti_2O_7Cl_4$ at 100 Hz & 1 kHz

3.3 Ferroelectric properties

Hysteresis loop is one important measure to confirm the material to be ferroelectric. The loop can then be used obtain a rough estimate of the spontaneous polarization [37]. The hysteresis loop can also be used to obtain information on domains, internal bias field, and other factors. The hysteresis curve between the electric field and electric polarization (P–E curve) of doped $Ba_5Ti_2O_7Cl_4$ single crystals is shown in Fig. 6. The hysteresis measurements of the samples are carried out at room temperature using computer controlled automatic P-E loop tester having specification TF-Analyser 2000E from IIT Bombay. For these measurements, samples were prepared in the form of crystal having an area about 18.36 mm^2 and thickness of 1.39 mm. The opposite faces consisted of electrodes with conducting silver paste. It was capable of carrying the sample's hysteresis measurement at room temperature at a frequency of 100 Hz. A saturated rectangular hysteresis loop was observed, indicating a good ferroelectric nature. The hysteresis loop is a typical square that is found in the applied field's domain switching [38]. The polarization-field (P–E) hysteresis loop of the ferroelectric single crystal is shown in Fig. 6. The polarization loops of $Ba_5Ti_2O_7Cl_4$ are well-developed showing large value of remnant polarization, P_r. which confirms that $Ba_5Ti_2O_7Cl_4$ is a normal ferroelectric phase. The symmetric hysteresis loop with the field that is typical for a phase containing long-range corporations between dipoles could be observed. The doped $Ba_5Ti_2O_7Cl_4$ single crystal indicates that the ferroelectric behaviour in the sample was greatly reduced. The rate of defect migration was probably due to low doping is low, thus creating an inner biased field that reversed the switched polarisation [39, 40]. In order to maintain the charge neutrality, oxygen vacancies [41] were shared with nearby unit cells. These oxygen vacancies will pin the domain wall motion and make the crystal hard, resulting in weaker ferroelectric properties [42]. The spontaneous polarizations Ps and coercive field Ec value of doped $Ba_5Ti_2O_7Cl_4$ a single crystals grown via the flux method with values of 2.26×10^{-4} C /m^2 and 2261 V /cm, respectively. The spontaneous polarizations Ps increases to 5.88×10^{-4} C /m^2 at E_c =4029 V/cm which shows good storage capacity of ferroelectric material $Ba_5Ti_2O_7Cl_4$.

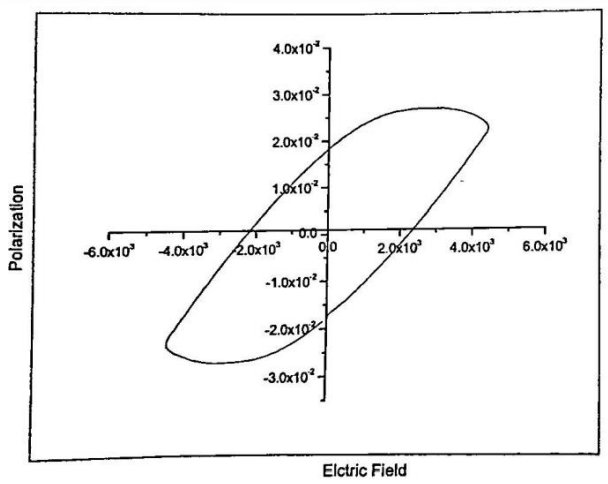

Fig 5 P–E hysteresis loop of doped $Ba_5Ti_2O_7Cl_4$ single crystal

4 Conclusions

Cr-doped $Ba_5Ti_2O_7Cl_4$ single crystal can be successfully grown by using high temperature solution growth technique i.e. the flux method. This method produces good quality, large size single doped $Ba_5Ti_2O_7Cl_4$ single crystal crystals. Finding of lattice parameters clearly indicates orthorhombic crystal structure with slight variation in a, b, c values with a well-matched structure resulting from the DTA. The doping do not show changes in lattice parameters i.e. there is no effect of impurity on structural properties. It allows for calculations of the lattice parameters of the as-grown crystal. Thermoanalysis of crystal with impurity shows two structural changes at 75-80^{o}C, 10-200^{o}C and ferroelectric transition at around 900^{o}C. Dielectric studies are very important for the determination of dielectric properties, such as dielectric constants and loss tangents. The dielectric constant with respect to temperature reveals phase transition and Curie temperatures showing that doping hardly has any effect on phase transition temperature. This is also in well agreement with thermo-analytical studies. When the dielectric loss tangent plotted against temperature, provides insight into the material's electrical behaviour. The dielectric studies showed a peak value of the dielectric constant at about 910 °C, thus indicating the Curie temperature of the material. Thus, it can be concluded that the dopants and the amount we used in our experiments would not change phase transition and Curie temperatures compared to pure $Ba_5Ti_2O_7Cl_4$-single crystals. The appreciable low dielectric loss with variable electric field indicates for the usefulness of material as a dielectric. The ferroelectric hysteresis loops showed good symmetry with the applied voltage, suppressing the effect of the internal field. These curves indicate that the ferroelectric sample presented typical ferroelectric material characteristics, and the dielectric behaviours of these materials could be due to space charge polarization. The direction of the spontaneous polarization vector may be switched between those orientations by an electric field representing switching in ferroelectric material is the occurrence of the ferroelectric hysteresis loop.

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