2.1 INTRODUCTION

Barium calcium titanate (Ba$_{1-x}$Ca$_x$TiO$_3$: BCT), a perovskite ferroelectric material, is a mixed solid solution of BaTiO$_3$-CaTiO$_3$. This material finds extensive application in electronic industry as a capacitor material. Many commercial applications employ barium titanate with a doping of either calcium or strontium (Mcquarrie 1955). Because of the considerable variation in its structural and physical properties with respect to barium titanate, BCT receives great interest both in ceramic and in single crystal forms. Extensive work has been carried out on the structural and physical properties of barium calcium titanate ceramics and only a few reports are available on the growth of BCT single crystals (Balakumar et al 1993a; 1994). Recently there has been a growing interest in materials possessing Diffused Phase Transition (DPT) (Tiwari et al 1989). BCT is one of the materials having diffused phase transition behaviour. Earlier studies report many controversial results regarding the site occupancy of Ca and the phase transition upon Ca doping. Hence, a detailed investigation is required to understand the site occupancy and the physical properties of BCT. This chapter gives details on the growth procedure, surface morphology, X-ray diffraction and dielectric studies on BCT single crystals.
2.2 STRUCTURE

Barium calcium titanate possesses perovskite structure. The structure can be considered as a rigid grouping of oxygen octahedra linked at the corners by shared oxygen ions. The Ti$^{4+}$ ions lie at the centre of each octahedron. Many of the properties of barium titanate family materials are determined by these TiO$_6^{8-}$ octahedra (Lines and Glass 1977). The general perovskite structure is shown in the Figure 2.1. As shown in the figure, the larger cations (Ba & Ca) occupy the corners of the cube. The smaller cations (Ti) occupy the body centre and the anions occupy the face centres.

2.3 PHASE DIAGRAM

The phase diagram of the BCT system has been studied by several groups. BaTiO$_3$-CaTiO$_3$ is not a complete solid solution and it has solubility over a restricted region as shown in Figure 2.2 (De Vries and Roy 1955). The single phase regions of BaTiO$_3$ and CaTiO$_3$ lie in between the two phase regions. Kwestroo and Paping (1959) studied the ternary phase diagram of BaO-CaO-TiO$_2$ at 400°C (Figure 2.3). It was reported that from the solid solution of Ba$_{1-x}$Ca$_x$TiO$_3$ various other phases of Ba-Ca-Ti-O system can be derived. Mcquarrie (1955) reported the ternary phase diagram of barium-calcium-strontium-titanate as shown in Figure 2.4. Here the two phase regions are found to be roughly a semi circle for about 20 mol.% of Ba to 20 mol.% of Ca along the edge of the system and into the interior upto 18 mol.% of Sr. The exact limits vary with the temperature. Also it is important to note that the firing temperature plays a major role in deciding the solubility of Ca in Ba. Hennings and Schreinemacher (1977) reported that there is a decrease in solubility of Ca in Ba when Zr is substituted in Ti site.
Figure 2.1  General ABO$_3$ perovskite structure
Figure 2.2 Phase diagram of BaTiO$_3$ - CaTiO$_3$
Figure 2.3  Ternary phase diagram of BaO-CaO-TiO₂
Figure 2.4  Ternary phase diagram of Barium-Calcium-Strontium-Titanate
2.4 POWDER PREPARATION

For the growth of BCT single crystals, one has to carefully prepare the precursor. The preparation of precursor controls the site occupancy of Ca and the site occupancy plays an important role in the physical and structural properties of BCT single crystals. Several groups have synthesized BCT powders by different techniques. Thermochemical reaction (Mitsui and Westphal 1961; Cooke et al 1966; Hennings and Schreinemacher 1977), dry route (Krishna et al 1993), semi wet route (Tiwari et al 1989), liquid mixing technique (Zhuang et al 1987) solid state reaction and chemical coprecipitation technique using chlorides (Krishna et al 1993) were tried. According to Tiwari et al (1991), if the atomic percentage of Ba+Ca is greater than that of Ti, the local stoichiometric variations occur forcing Ca ions to occupy Ti site. Later it was confirmed by neutron diffraction that all Ca ions occupy only Ba site in the case of crystals grown by flux technique using the precursor of BaCO₃, CaCO₃ and TiO₂ (Rajagopal et al 1994; Sastry et al 1996).

2.5 CRYSTAL GROWTH

In the present work single zone resistive heated furnace with a vertical temperature gradient of 3-4°C/cm and an axial gradient of 2-3°C/cm was used. Thermal stability was achieved by using an Eurotherm PID controller (Model 818 P) equipped with a phase angle fired thyristor (Model 461). The purity of the chemicals is crucial for the size and quality of the crystals to be grown. In the present work, ALDRICH make chemicals with purity; BaCO₃-99.995%, CaCO₃-99.95%, TiO₂-99.9% and KF-99.9% were used. Owing to the corrosive nature of potassium fluoride flux, quartz and alumina crucibles were not successful and only platinum crucibles could be used. The crucibles were having smooth walls in order to avoid spurious nucleation.
The crystal growth was carried out by two methods. In the first method, the precursors were prepared separately and then mixed with the flux before loading into the furnace for growth. In the second method, accurately weighed BaCO₃, CaCO₃ and TiO₂ powders were calcined at 1000°C for 5 hours. After calcination the powders were thoroughly ground and then mixed with potassium fluoride and taken in a 100 cc crucible and loaded into the furnace. In both the cases, the furnace was heated to 1180 to 1225°C, soaked for a few hours and then slow cooled to 800°C/hr at a rate of 1-5°C/hr. Then the furnace was cooled to room temperature at a rate of 75°C/hr. The crystals were separated from the flux by dissolving in hot water. The growth parameters were optimized for different concentrations of Ca by changing the flux-charge ratio, cooling rate and soaking period.

Crystals were grown with starting compositions of 8, 12, 16, 18 and 20 mol.% of Ca. For lower concentrations of Ca (8 and 12 mol.%), relatively fast cooling rate (4-7°C/hr) was used. For lower concentrations of Ca, butterfly twins (Figure 2.5a) were obtained for a soaking period of 8 hours and a cooling rate of 4-7°C/hr (Varatharajan et al. 1998). This type of butterfly morphology is generally observed for barium titanate single crystals and is due to low stacking fault energy (Nielsen et al. 1962). In order to reduce the twin formation, the soaking period was increased to 12 hours and the cooling rate was reduced to 2-5°C/hr. With these conditions, the twin formation was completely reduced and platy crystals were obtained (Figure 2.5b). When the cooling rate was further reduced to 1-2°C/hr, a bulk mass of tiny crystals was obtained and it was very difficult to separate individual crystals.

For higher concentrations of calcium (16, 18 and 20 mol.%), initially for relatively less soaking period, small size crystals were obtained. In order to improve the size and quality of the crystals the cooling rate was reduced to 1°C/hr and large size crystals of dimension 5 x 5 x 4 mm³ were obtained. The problem in adopting a very slow cooling rate is the evaporation of flux. Most of the times,
Figure 2.5a  Butterfly twin of $\text{Ba}_{0.88}\text{Ca}_{0.12}\text{TiO}_3$

Figure 2.5b  Platelet crystal of $\text{Ba}_{0.88}\text{Ca}_{0.12}\text{TiO}_3$

Figure 2.5c  Single crystals of $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$
though the crucible was tightly closed with a platinum lid, it was found that a large amount of potassium fluoride is lost. To avoid the flux evaporation, the flux was taken in the crucible first, and the charge was loaded over the flux. In that case also, incredible flux evaporation was observed. To overcome this problem excess flux was employed. Crystals of size 5 x 5 x 4 mm$^3$ (Figure 2.5c) were grown. The optimized growth parameters for different concentrations of Ca are given in Table 2.1 (Varatharajan et al 1998).

**Table 2.1**

Optimized growth parameters for Ba$_{1-x}$Ca$_x$TiO$_3$ single crystals

<table>
<thead>
<tr>
<th>Starting composition</th>
<th>Flux-charge ratio</th>
<th>Growth temperature (°C)</th>
<th>Soaking period (hrs) / cooling rate (°C/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba$<em>{0.92}$Ca$</em>{0.08}$TiO$_3$</td>
<td>70:30</td>
<td>1180</td>
<td>8/4 –7</td>
</tr>
<tr>
<td>Ba$<em>{0.88}$Ca$</em>{0.12}$TiO$_3$</td>
<td>75:25</td>
<td>1180</td>
<td>12/3 –5</td>
</tr>
<tr>
<td>Ba$<em>{0.84}$Ca$</em>{0.16}$TiO$_3$</td>
<td>80:20</td>
<td>1200</td>
<td>15/2–4</td>
</tr>
<tr>
<td>Ba$<em>{0.82}$Ca$</em>{0.18}$TiO$_3$</td>
<td>80:20</td>
<td>1100</td>
<td>20/1–3</td>
</tr>
<tr>
<td>Ba$<em>{0.80}$Ca$</em>{0.20}$TiO$_3$</td>
<td>82:18</td>
<td>1225</td>
<td>24/1–2</td>
</tr>
</tbody>
</table>

2.6 SURFACE MORPHOLOGY

To study the growth mechanism, the grown crystals were viewed through an optical microscope (Leitz Wetzler). Three types of morphology were observed on the grown crystals.

(i) vein like structure

(ii) concentric spiral pattern

and (iii) hopper structure

The vein structure (Figure 2.6a) is generally observed on the barium titanate single crystals (Balakumar et al 1993 b). These types of vein structures are like
Figure 2.6  Surface morphology of $\text{Ba}_{1.5}\text{Ca}_{x}\text{TiO}_3$ (a) vein structure, (b) concentric spiral growth pattern and (c) hopper structure
Veins in leaf, spreading over the entire surface of the crystal. Vein structures were observed on the butterfly twinned crystals and on the platy crystals with lower concentrations of calcium. This type of veins occur because of low stacking fault energy and also due to lower supersaturation. The vein pattern was not observed on the crystals with higher concentrations of calcium. Concentric spiral growth pattern (Figure 2.6b) was observed on the crystal grown with 20 mol.% of Ca. This type of concentric growth pattern occurs due to the screw dislocation and higher supersaturation (Marella et al 1994). The hopper structure (Figure 2.6c) occurs when the crystals grow at the surface of the melt. In this case only the edge of the crystal is in contact with the melt. So the crystal grows only at the edge and creating a depression at the centre (Varatharajan et al 1998; Elwell and Scheel 1975). This type of structure can be avoided by adopting very slow cooling rate throughout the growth regime.

2.7 X-RAY DIFFRACTION STUDIES

2.7.1 Laue pattern

To confirm the single crystallinity of the grown crystals, back reflected Laue photograph was taken (Figure 2.7). The spots occurred at definite positions, which are determined by the wavelength of the X-ray, size and orientation of the unit cell, and the intensity of the blackening varies from one spot to another. The size and shape of the spots in the back reflected Laue photograph provide a simple means of assessment of the perfection of the crystal. The spots in the Figure 2.7 confirm the good quality of the crystal.
Figure 2.7 X-ray Laue back reflection photograph of $\text{Ba}_{0.8}\text{Ca}_{0.2}\text{TiO}_3$ crystal
2.7.2 Powder X-ray diffraction studies

To confirm the structure and to estimate the variation in lattice parameters for different concentrations of Ca, powder X-ray diffraction studies were carried out. Many crystals were crushed and fine powder was used for the diffraction experiments. Powder X-ray patterns were recorded using Rich Seifert X-ray diffractometer. Figures 2.8 a, b, c & d show the powder X-ray pattern of BCT crystals with 8, 12, 16 and 20 mol.% of Ca. From the figures, it is evident that the crystals possess tetragonal structure. The cell constants and cell volume for different concentrations of Ca were calculated and tabulated in table 2.2. The lattice parameters and the cell volume decreased on increasing Ca concentration. The c/a ratio also decreased on increasing Ca concentration (Varatharajan et al 1998). This shows that the system shifts to cubic phase from tetragonal phase. This decrease in lattice parameters and cell volume is due to low ionic radius of Ca compared to Ba and occupation of Ca ions in Ba site.

2.8 ELECTRON SPECTROSCOPY FOR CHEMICAL ANALYSIS (ESCA)

To confirm the valence state of Ca, XPS studies were performed on the crystal grown with 12 mol.% of Ca. ESCA is one of the powerful techniques for the element identification and its valence state. Surface analysis by X-ray photoelectron spectroscopy (XPS), more commonly known as electron spectroscopy for chemical analysis, is accomplished by irradiating the sample with soft X-rays and analyzing the energy of the electrons emitted. MgKα X-rays (1253.6 eV) or AlKα X-rays (1486.6 eV) are commonly used. These photons have limited penetrating power in solids of thickness of the order of 1-10 μm. The photons interact with atoms in the surface region by photoelectric effect, causing electrons to emit. The emitted electrons possess kinetic energies given by

\[ KE = hv - BE - \phi, \]
Figure 2.8 Powder X-ray diffraction pattern of (a) $\text{Ba}_{0.92}\text{Ca}_{0.08}\text{TiO}_3$, (b) $\text{Ba}_{0.88}\text{Ca}_{0.12}\text{TiO}_3$
Figure 2.8  Powder X-ray diffraction pattern of (c) $\text{Ba}_{0.84}\text{Ca}_{0.16}\text{TiO}_3$, (d) $\text{Ba}_{0.8}\text{Ca}_0.2\text{TiO}_3$
where $h\nu$ is the energy of the photon, $BE$ is the binding energy of the atomic orbital from which the electron originates and $\phi_s$ is the spectroscopic work function. The binding energy is regarded as the ionization energy of the atom for the particular shell.

Figure 2.9 shows the XPS spectrum of Ca ions which confirms the valence state as $2^+$. As shown in figure, the Ca ions have binding energies released by 2p orbital. It contains two splittings one at 346 eV and another at 349.5 eV separated by 3.5 eV which is in good agreement with the literature values (Wagner et al 1991).

2.9 FERROELECTRIC STUDIES
2.9.1 Hysteresis studies

The basic property for the identification of a ferroelectric material is the hysteresis loop. The perfection of the loop infers the quality of the crystal grown. The loop gives a measure of spontaneous polarization that can be reversed. A Sawyer–Tower circuit as shown in Figure 2.10 is generally employed to study the hysteresis (Burfoot and Taylor 1979). High fields applied across the sample at a frequency of 50 Hz cause polarization reversal. The P-E hysteresis loops were traced using Sawer-Tower circuit. Figures 2.11a, b and c show the hysteresis loops observed for the crystals grown with 12, 16 and 20 mol.% of Ca. The Y-scale is the measure of the polarization and X-scale is the applied field. It can be seen that the loops are perfect and are indicative of good quality, strain free single crystal. The spontaneous polarization values for different concentrations of Ca have been calculated using the formula $P_s = \frac{V_o C_o}{S}$, where $V_o$ is the electric field, $C_o$ is the internal capacitor of the instrument and $S$ is the surface area of the sample. The spontaneous polarization ($P_s$) values decrease on increasing Ca concentration and this decrease is due to the antiferroelectric nature of CaTiO$_3$ (Varatharajan et al 1999 a). The values of $P_s$ are tabulated in table 2.2.
Figure 2.9  XPS spectrum of Ca$^{2+}$ ions
Figure 2.10  Sawer - Tower circuit for observing hysteresis
Figure 2.11  Hysteresis loops of (a) $\text{Ba}_{0.88}\text{Ca}_{0.12}\text{TiO}_3$,
(b) $\text{Ba}_{0.84}\text{Ca}_{0.16}\text{TiO}_3$ and (c) $\text{Ba}_{0.8}\text{Ca}_{0.2}\text{TiO}_3$
2.9.2 Domain structure studies

One of the important characteristics of a ferroelectric material is the existence of ferroelectric domains. As discussed in the chapter 1, ferroelectric materials possess spontaneous polarization with different orientations of the dipoles. A region of uniform alignment of dipoles is known as a domain. When a crystal is cooled from a paraelectric phase to a ferroelectric phase in the absence of external electric field, there are at least two equivalent directions along which the spontaneous polarization may occur. In order to minimize the energy associated with the depolarization field, different regions of the crystal polarize in each of these directions and each volume of uniform polarization is referred as a domain (Lines and Glass 1977). From the crystallographic point of view the domain structure is analogous to twin structure.

A ferroelectric domain is a homogeneous region in a ferroelectric crystal. In each domain the polarization is in a different direction. The demarcation between two domains is called domain wall. It is electrically neutral and corresponds to minimum free energy. The crystal lattice remains coherent through a domain wall, although it may be distorted by the wall (Burfoot 1967). If the spontaneous polarization $P_s$ is normal to the most developed faces, the domains are referred as $c$-domains and when $P_s$ is parallel to the observed surface and perpendicular to the polarization direction of $c$-domains, the domains are referred as $a$-domains. Various types of domains observed in ferroelectric materials are schematically shown in Figure 2.12 (Yamamoto et al 1997).

The formation of domain pattern is determined by the conditions of the transition from the paraelectric to ferroelectric phase and the structural changes between two phases. The 90° domains are the important factor affecting the physical properties of the most ferroelectrics (Eknadiosyants et al 1997).
Figure 2.12 Schematic of different domain structures in Ferroelectric materials
The domains can be observed depending on many factors such as crystal symmetry, electrical conductivity, defect structure, magnitude of spontaneous polarization and the method of crystal preparation and sample size (Lines and Glass 1977). Since the discovery of domains, several techniques have been developed to study the domain structure in ferroelectric materials. They include etching, powder technique (Aristo et al 1983), X-ray topography, polarizing microscopy, scanning electron microscopy and atomic force microscopy. Techniques like etching and powder deposition modify the surface of the crystals and it is very difficult to use the samples for further studies. Another factor concerns the limit of resolution of these methods. Both these methods have the disadvantage of either having low magnification or destruction of the samples. In the case of SEM and TEM electron charging effect comes into play and need stringent sample preparation. Compared to other methods, AFM has many advantages with a wide range in X-Y direction and high measurement resolution in the Z-direction. This technique has become a promising tool to observe the morphology of the materials without any surface treatment. In particular, the development of piezoelectric scanners enables to observe surfaces over a wide scan range. This is advantageous for the observation of ferroelectric domains ranging from the nanometer to micrometer scale with required resolution along the Z-direction. This technique has been successfully used for the observation of ferroelectric domains (Hamazaki et al 1995; Takashige et al 1996; 1997 a; 1997 b; Balakumar et al 1997).

In the present work, the domain patterns were observed on BCT single crystals using an AFM (Digital Instruments Inc., Nanoscope II) operated in the static contact mode at room temperature. The maximum allowed area for the scan head was 960 x 960 nm². Si cantilevers having integrated tips with spring constants of about 0.063 - 0.65 N/m were used. As grown crystals of size 5 x 5 x 1 mm³ were used for the observation.
Figure 2.13 a shows the AFM image of $90^\circ$ c- domains. BCT single crystals undergo ferroelectric transition from high temperature cubic phase to low temperature tetragonal phase with $P_s$ along the c- axis. Thus the tetragonal crystal has adjacent regions which are polarized at $90^\circ$ to each other called $90^\circ$ domains. Figure 2.13 b shows the another type of $90^\circ$ domains. Figure 2.13 c shows the two dimensional $90^\circ$ c- domains (Varatharajan et al 1999 a). The figures show that the domains are well defined and confirm the good quality of the crystals with smooth surface.

2.9.3 Dielectric studies

Several researchers have studied the dielectric behaviour of BCT ceramics. But the reports are controversial leading to inconclusive results about the dielectric and phase transition of BCT. Berlincourt and Kulesar (1952) reported that Ca doping on barium titanate causes only a negligible change in Curie point. Later it was reported that the phase transition temperature increases for lower concentration and decreases for higher Ca content and the transition is sharp. Zhuang et al (1987) reported that the addition of very small amount of Ca$^{2+}$ ions at Ti$^{4+}$ site leads to a diffused phase transition and significantly lowers the Curie temperature. Subsequently, on contrary to the report of Zhuang et al (1987), Tiwari et al (1989) reported, for BCT ceramics, that the Curie temperature increases on Ca doping and also the transition becomes diffused when Ca$^{2+}$ ions replace Ba$^{2+}$ ions. Pandey et al (1992) reported that, if Ca$^{2+}$ ions enter into both Ba$^{2+}$ and Ti$^{4+}$ sites, there is no appreciable change in Curie temperature. When Ca$^{2+}$ ions occupy only Ba$^{2+}$ site, the Curie temperature increases and the transition becomes diffused. Hence a detailed dielectric studies on single crystals of BCT are required to predict the nature of phase transition, Curie temperature and the value of dielectric constant.

Dielectric constants were measured using an Impedance analyzer (Solatron 1260) at different frequencies and various temperatures after annealing the crystal and...
Figure 2.13 (a) and (b) AFM image of 90° domains and (c) two dimensional domain structure.
electroding with silver. From the dielectric studies it is found that the Curie temperature increases on increasing the Ca concentration. Figures 2.14, 2.15, 2.16 and 2.17 show the temperature Vs dielectric constant for crystals grown with 8, 12, 16 and 20 mol. % of Ca at different frequencies. The dielectric constant is found to decrease for higher concentration of Ca and this is due to the antiferroelectric nature of CaTiO₃ (Varatharajan et al 1998; Verbitskaya et al 1988)

The Curie point exists over a range of temperature unlike the BaTiO₃ in which the Curie point exists at a definite temperature. This type of transition is termed as diffused phase transition. The mechanism for the diffused phase transition (DPT) is not well understood so far. Smolensky (1970) proposed an inhomogeneity model in which different micro-regions on a scale of a few thousandths of the sample are believed to possess different Tc’s because of the compositional variation from one micro-region to another. The average value of Curie temperature for all the micro-regions leads to the diffused nature. Later it was shown that the DPT occurs because of the intrinsic disorder effect introduced by the replacement of A or B site cation in the perovskite structure (Burns 1976). The occurrence of DPT was attributed to the clamping of ferroelectric domains between ferroelectric and paraelectric phases (Tiwari et al 1991). Also it was confirmed in the case of BCT ceramics that this diffused nature of transition occurs only when the Ca ions exclusively occupy the Ba site (Krishna et al 1993).

In the present work, the diffused nature is found to be increased on increasing the Ca concentration i.e. for 20 mol. % of Ca the Curie temperature exists over a range of temperature (between 432 and 438 K). At higher concentrations of calcium, it is very difficult to predict the exact Curie temperature because of the increasing diffusivity. The diffused phase transition observed in the BCT single crystals is in agreement with the observations made on the ceramic samples. The Curie temperature for different concentrations of Ca are given in table 2.2.
Figure 2.14  Dielectric constant Vs Temperature for Ba$_{0.92}$Ca$_{0.08}$TiO$_3$
Dielectric Constant ($\varepsilon'$) vs. Temperature for $\text{Ba}_{0.88}\text{Ca}_{0.12}\text{TiO}_3$

Figure 2.15  Dielectric constant Vs Temperature for $\text{Ba}_{0.88}\text{Ca}_{0.12}\text{TiO}_3$
Dielectric Constant ($\varepsilon'$)

Figure 2.16  Dielectric constant Vs Temperature for Ba$_{0.84}$Ca$_{0.16}$TiO$_3$

Temperature (K)

Dielectric Constant ($\varepsilon'$)
Figure 2.17  Dielectric constant Vs Temperature for Ba$_{0.8}$Ca$_{0.2}$TiO$_3$
To study the phase transition at low temperatures, dielectric constants were measured up to 150 K for crystals with 12 and 20 mol.% of Ca. Figures 2.18 and 2.19 show the temperature Vs dielectric constant for 12 and 20 mol.% of Ca at low temperatures. These studies reveal that the phase transition temperature of orthorhombic phase is shifted to 272 K from 286 K (for pure BaTiO₃) and for the rhombohedral phase it is shifted to 180 K from 193 K for 12 mol.% of Ca. For 20 mol.% of calcium, both orthorhombic and rhombohedral phases disappear and only the tetragonal phase exists up to 150 K (Varatharajan et al. 1999a).

Table 2.2

<table>
<thead>
<tr>
<th>Starting composition</th>
<th>Lattice parameters</th>
<th>Cell volume</th>
<th>( P_s ) (( \mu )c/( cm^2 ))</th>
<th>Tc (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Ba_{0.92}Ca_{0.08}TiO_3 )</td>
<td>3.997 4.041</td>
<td>64.215</td>
<td>10.2</td>
<td>135</td>
</tr>
<tr>
<td>( Ba_{0.84}Ca_{0.16}TiO_3 )</td>
<td>3.991 4.037</td>
<td>63.552</td>
<td>6.18</td>
<td>140</td>
</tr>
<tr>
<td>( Ba_{0.80}Ca_{0.20}TiO_3 )</td>
<td>3.980 4.015</td>
<td>63.467</td>
<td>4.6</td>
<td>154</td>
</tr>
<tr>
<td>( Ba_{0.80}Ca_{0.20}TiO_3 )</td>
<td>3.976 3.997</td>
<td>63.348</td>
<td>2.7</td>
<td>162</td>
</tr>
</tbody>
</table>

2.10 OPTICAL STUDIES

The transmission and absorption spectra were taken for the crystal grown with 12 mol.% of Ca after lapping into 1 mm thickness and polished with a 6 micron diamond paste. From the transmission and absorption spectra, the refractive index and absorption coefficient were calculated with respect to the wavelength and photon energy.
Figure 2.18  Dielectric behaviour of $\text{Ba}_{0.88}\text{Ca}_{0.12}\text{TiO}_3$ at low temperature

Figure 2.19  Dielectric behaviour of $\text{Ba}_{0.8}\text{Ca}_{0.2}\text{TiO}_3$ at low temperature
The transmission and absorption spectra are shown in Figures 2.20a and 2.20b respectively. The transmittance is found to be 45% and this low value may be due to the fact that the crystals are grown from flux and the absorption is also high. From the transmission and absorption spectra the refractive index was calculated using the formula

\[ n = \frac{1+R^{1/2}}{1-R^{1/2}} \]

where \( R \) is the reflection and the absorption coefficient is calculated using the formula

\[ \alpha = \log\left(\frac{T}{(1-R)^2}\right)/d \]

where \( d \) is the thickness of the sample and \( T \) is the transmittance.

The refractive index values depicted in Figure 2.21 are found to be less compared to pure BaTiO\(_3\) (for pure BaTiO\(_3\) \( n_a=2.66\)) and this may be due to the occupation of calcium in the barium site and also impurities present in the crystal (Varatharajan et al. 1998). The impurities may be platinum due to the contamination from the crucible material. The absorption coefficient is found to be higher for calcium doping compared to pure BaTiO\(_3\) as shown in Figure 2.22.

2.11 CONCLUSION

Bulk single crystals of barium calcium titanate have been grown from KF flux by eliminating the butterfly twin formation. It is found that Ca substitution hinders the hexagonal phase and hence the twin formation. Surface morphology studies on the as-grown crystals reveal the spiral and hopper growth mechanism. The single crystallinity and the structure of the grown crystals were confirmed by Laue and powder X-ray diffraction studies. The lattice parameter values are found to
Figure 2.20  (a) Transmission and (b) Absorption spectra for $\text{Ba}_{0.88}\text{Ca}_{0.12}\text{TiO}_3$
Figure 2.21 Refractive index Vs Wavelength for $\text{Ba}_{0.88}\text{Ca}_{0.12}\text{TiO}_3$
Figure 2.22  Absorption coefficient Vs Photon energy for $\text{Ba}_{0.86}\text{Ca}_{0.12}\text{TiO}_3$
decrease on increasing Ca concentration. The valence state of Ca has been confirmed by XPS studies.

90° c-domains were observed by atomic force microscopy. The spontaneous polarization values calculated from hysteresis measurements are found to decrease on increasing Ca concentration due to the substitution of antiferroelectric CaTiO₃ in ferroelectric BaTiO₃. The Curie temperature increases while increasing the Ca concentration and the transition becomes diffused. The diffused nature becomes more prominent for higher concentrations of Ca. The refractive index values estimated from transmission and absorption spectra decrease on Ca substitution.