CHAPTER 5

GROWTH OF ABO₃ PEROVSKITE FERROELECTRIC SINGLE CRYSTALS AND THEIR CHARACTERIZATION

5.1 INTRODUCTION TO ABO₃ PEROVSKITE FERROELECTRICS

The ABO₃ perovskite oxides have been of continuing interest because of their ferroelectric and electro-optic properties. The perovskite structure occupies a prominent place among all the known ternary systems of composition ABX₃. The ferroelectric oxygen-octahedra make the compounds attractive for optical device applications. This is not only due to its wide occurrence but also to its interesting and useful properties associated with structure. The name perovskite stems from the rare mineral CaTiO₃ which possesses a simple cubic structure with a point group m3m.

Most of the useful ferroelectrics have perovskite structure. These oxides have an extremely simple structure with general chemical formula ABO₃ where O is the oxygen, A represents a cation with a larger ionic radius and B cation with a smaller ionic radius (Figure 5.1a). In the cubic state it has the A atoms at the cube corners, B atoms at the body center and the oxygen at the face centers. Most of the ferroelectrics with perovskite type structure are compounds with either A²B⁴O₉ or A¹B⁵O₅ type formula.

The structure can also be regarded as a three dimensional network of BO₆ octahedra arranged in a simple cubic pattern and linked together by shared oxygen atoms, as shown in Figure 5.1b. Hence it may also be regarded as a cubic close packed arrangement of A and O ions with B ions filling the octahedral interstitial positions. Oxygen octahedra have much technological importance due to the non-
Figure 5.1a  The cubic ABO$_3$ perovskite structure

Figure 5.1b  Three dimensional network of BO$_6$ octahedra in the cubic structure
linear behaviour in piezoelectricity, pyroelectricity, ferroelectricity, superconductivity, ferromagnetism properties and their applicability in devices.

A wide variety of cation can be substituted in the perovskite structure. The relationship

\[ t = \frac{(R_A + R_o)}{2(R_B + R_o)} \]

describes the ideal cubic structure where \( t = 1.0 \) and \( R_A, R_B, \) and \( R_o \) indicate the ionic radius of large cation (A), small cation (B) and anion (oxygen) respectively. The preparation of solid solutions, solubility regions and their physical properties have been extensively reviewed by Jaffe et al (1971). Since the discovery of BaTiO₃ and PbTiO₃, enormous efforts have been taken to study the properties of compositional modified ceramic materials and single crystals.

In the present work, growth and characteristics of three members of the room temperature tetragonal perovskite ferroelectric family viz., \( \text{BaTiO}_3 \), \( \text{PbTiO}_3 \) and \( \text{PbCaTiO}_3 \) (PCT) crystals are presented. \( \text{BaTiO}_3 \) crystals were grown by the standard Remeika's technique and \( \text{PbTiO}_3 \) and its solid solution \( \text{PbCaTiO}_3 \) crystals were grown by using PbO as a flux. Effect of solvent-solute ratio, soaking temperature and cooling rate is also discussed.

5.2 BARIAUM TITANATE

The first ferroelectric perovskite discovered was \( \text{BaTiO}_3 \). The compound of the formula \( \text{BaTiO}_3 \) has probably attracted more scientific attention in the past few decades. It was the first ferroelectric perovskite discovered without hydrogen atoms and with more than one ferroelectric phases (Godefroy and Jannot 1992). The polar nature of \( \text{BaTiO}_3 \) leads to a variety of well known applications, including piezoelectric and pyroelectric properties. It exhibits high electro-optic coefficient
which is useful in applications such as waveguide modulator or switcher. This crystal was considered to be the best one for photorefractive applications because of its large electrooptical coefficient (Ducharme and Feinberg 1986). BaTiO₃ is a highly nonlinear optical material which has been used for optical phase conjugation, image processing and laser resonators (Klein and Schwartz 1986). It has high beam coupling gain and short beam-coupling rise time. It can be operated at visible and near-infrared regions and good for four-wave mixing with milliwatts optical power.

5.2.1 Structure

BaTiO₃ has the prototype cubic perovskite structure (point group m3m) when the temperature is above 120°C (Curie point). When the temperature is between 120°C and 0°C, it is ferroelectric and has stable tetragonal phase (point group 4mm) with $c/a$ ratio of about 1.01. The direction of spontaneous polarization is along the $c$-axis of the tetragonal unit cell. As the temperature falls below 0°C, a new phase having orthorhombic point group (mm2) becomes stable. This phase is also ferroelectric with the spontaneous polarization parallel to the [110] direction in the original cubic structure. At -90°C the third phase transition occurs and the lattice symmetry changes upon cooling from orthorhombic to rhombohedral. Above 1460°C the structure transforms to hexagonal form.

In the cubic unit cell shown in Figure 5.1a Ba are at the body corners, the oxygen anions are at the face centres and titanium ions are in the octahedral void at the body centre. Only one out of four octahedral voids in the unit cell is occupied and this corresponds to their chemical formula, with one titanium for every four species of the other kinds: one barium plus three oxygen. The tetragonal structure of BaTiO₃ is shown in Figure 5.2a. The lattice constants in the tetragonal phase are $a=3.9928\,\text{Å}$ and $c=4.0388\,\text{Å}$. When a structural phase transition from cubic to tetragonal symmetry
Figure 5.2a  Tetragonal structure of BaTiO$_3$

Figure 5.2b  The displacement of Ba$^{2+}$, Ti$^{4+}$ and O ions along the c-axis
occurs $\text{Ba}^{2+}$, $\text{Ti}^{4+}$ and $\text{O}^{2-}$ ions are displaced from their original equilibrium lattice positions (Figure 5.2b).

### 5.2.2 Crystal growth - survey

The growth of optical quality $\text{BaTiO}_3$ crystals is very difficult, since $\text{BaTiO}_3$ has a hexagonal-to-cubic transition at 1460°C. Hence it is not possible to obtain good single crystals from $\text{BaTiO}_3$ stoichiometric melt. Flux growth technique is one among the ways for avoiding the hexagonal phase, many works have been done in this way with KF (Remeika 1954), $\text{BaCl}_2$ (Blattner et al 1947) as solvent. In principle, Top seeded solution growth (TSSG) technique gives pure $\text{BaTiO}_3$ crystals of good optical quality and big size (Godefroy et al 1977; Rytz et al 1990; Tomita 1991; Garrett and Mnushkina 1996).

The Remeika's technique (1954) for growing barium titanate single crystals was based on crystallization from a supersaturated solution with potassium fluoride flux. This technique has widespread acceptance because it is readily reproducible and always yield good single crystals. In this method the crystals grew as thin flakes. The choice of potassium fluoride as a solvent is a good one from the stand point of solubility of barium titanate. Figure 5.3 shows the partial phase diagram for the $\text{BaTiO}_3$-KF system. This phase diagram was reported by Karan and Skinner (1953) from differential thermal analysis measurements. Eventhough $\text{BaTiO}_3$ has cubic structure around its melting point it has large flat plate morphology when it is grown from KF solutions and the morphology is termed as butterfly twins. Already several investigations have been made to analyze this problem particularly with purity, variation in the crystal yield with particle size, soaking period, solvent-solute ratio, etc. Effect of foreign ions as additives to inhibit the butterfly morphology was also reported (Sholokhovich et al 1968).
Figure 5.3  BaTiO$_3$ - KF phase diagram
In the present work BaTiO$_3$ crystals were grown from KF by Remeika's technique. Due to the small volume of the crucible a two step process was adopted for chemical loading. Powder X-ray diffraction studies have also been carried out using a Rich Seifert Powder Diffractometer with CuK$_\alpha$ radiation ($\lambda=1.5418\text{Å}$).

5.3 LEAD TITANATE

Lead titanate is an important ferroelectric material having a perovskite structure similar to Barium titanate. This material is of great interest in high-frequency ultrasonic transducer and detector applications (Xu 1991). The electro-optic properties of PbTiO$_3$ for modulator applications have been reported by Fontana et al (1995). Lead titanate is generally considered as a text book example of a displacive ferroelectric phase transition. The transition is strongly of first order (Fontana et al 1988). It is having remarkable ferroelectric, pyroelectric and piezoelectric properties. The physical properties of the material have been extensively studied and the technological importance of the material in ceramic form has been demonstrated repeatedly in the literature (Xu 1991). Recently elastic, piezoelectric and dielectric properties of mono-domain single crystals of PbTiO$_3$ have been studied (Dai et al 1992; Li et al 1993a).

The properties of pure ceramic and single crystal PbTiO$_3$ have been difficult to study because of the high electrical conductivity (Jaffe et al 1971) and large tetragonal distortion that occurs at the ferroelectric to paraelectric transition (496°C). The dc conductivity also varies from $10^{-11}$ to $10^{-6}\text{ohm}^{-1}\text{cm}^{-1}$ (Remeika and Glass 1969; Fesenko et al 1972). Defects on the surface layer of the crystal also affect the permittivity and electrical conductivity of the crystals. Also the presence of defects may cause colouration of crystals and increase their electric conductivity making technical application of these crystals difficult or even impossible. In addition to this, growth of pure PbTiO$_3$ crystals is difficult because of the problems encountered due to the evaporation of PbO during the growth.
5.3.1 Structure

Above Curie temperature (490°C) PbTiO$_3$ has a simple cubic structure. The crystal structure is distorted at room temperature to a tetragonal lattice with $a=3.904\text{Å}$; $c=4.152\text{Å}$ and $c/a=1.063$. In the tetragonal phase the crystal is ferroelectric (space group P4mm). Both Pb and Ti atoms are displaced from their respective oxygen planes by 0.47Å and 0.30Å (Figure 5.4a) respectively. The displacements are in the [001] direction (Sicron et al 1994). The unit cell and the relative atomic displacements display a substantially larger distortion for PbTiO$_3$ than they do for BaTiO$_3$. The oxygen octahedra has no distortion while going to the ferroelectric phase unlike BaTiO$_3$ in which the oxygen and B-cations are shifted in the same direction relative to A-site. A schematic representation of the low-temperature phase with the Pb and Ti atoms at the center is shown in Figure 5.4b. The spontaneous polarization is around 81µC/cm$^2$ due to the large ionic shifts (Glazer and Mabud 1978). Hence it is a promising material for high temperature applications. Yet another transition occurs at 183K at which the crystal undergoes a transition to an orthorhombic phase with a very small change in the lattice parameters but remains ferroelectric (Kobayashi et al 1983).

5.3.2 Crystal growth - survey

The difficulty of growing lead titanate crystals from the stoichiometric melt and the unsatisfactory results of crystallization by hydrothermal method (Grabmaier 1976) induced researchers to opt for growth from solutions in salts and oxides with a low melting point. Most of the ferroelectric properties of PbTiO$_3$ single crystals reported in the literature were obtained from crystals grown by the flux method. Technological conditions for obtaining high quality PbTiO$_3$ single crystals were given by Wojcik (1988). Flux systems generally employed were Pb$_3$O$_4$-PbF$_2$ and KF-KBF$_4$-PbF$_2$, PbO-TiO$_2$-V$_2$O$_5$, Na$_2$SiO$_3$, PbCl$_2$ (Bhide 1962; Suchicital and Payne 1990).
Figure 5.4a  Crystal structure of tetragonal PbTiO$_3$

Figure 5.4b  Schematic representation of Ti and Pb ion environment in PbTiO$_3$
Growth with the above fluxes yielded very small (1-3mm³) isometric crystals of high conductivity and a complex domain structure. Thick plates of uranium-doped crystals were obtained by Remeika and Glass (1969). Later other fluxes were developed namely PbO (Kobayashi 1958; Sun et al 1993), PbO-B₂O₃ (Fesenko et al 1972; Turik et al 1979; Wojcik 1988; Li et al 1992; Oka et al 1996), KF (Bhide et al 1962 1968; Suchicital and Payne 1990). In these studies very thin and plate like single crystals upto 20mm in size were grown.

5.3.3 Phase diagram

The phase diagram of PbO-TiO₂ has been studied extensively (Eisa et al 1980). The system PbO-TiO₂ investigated by Eisa et al (1980) exhibited two eutectic temperatures, one a higher at 1240°C with 10% excess TiO₂ and another lower at 838°C (Figure 5.5a). The lower eutectic situated at the composition 15mol.% of TiO₂ + 85mol. % of PbO is of particular importance for flux growth experiments. The value of 838°C was taken as the lowest limit for the growth temperature. Recently Soh et al (1994) published a new phase diagram (Figure 5.5b) which has many disputes due to the existence of intermediate compound and allotropic transformation of TiO₂.

Although a considerable amount of work on the growth of lead titanate crystals has been carried out, these crystals were opaque and heavily twinned and not suitable for optical investigations. This induced to undertake a study of the crystallization of PbTiO₃ from self flux to study the domain dynamics. The choice of PbO is due to the fact that it has been demonstrated to be a suitable high temperature solvent for many oxides including perovskites (Garton and Wanklyn 1967; Nomura et al 1968; Brunskill et al 1982). In addition, PbO itself is a component of PbTiO₃ thus avoiding the incorporation of foreign ions into the crystal lattice.
Figure 5.5  Phase diagram of PbO-TiO$_2$
(a) Eisa et al 1980 and (b) Soh et al 1994
To understand the growth mechanism and surface morphology, the grown crystals were studied using an optical microscope using reflection mode. Powder diffractometer patterns were recorded by using Rich Seifert diffractometer with CuK$_\alpha$ ($\lambda$=1.5418Å) radiation on the samples prepared by grinding several crystalline blocks.

5.4 LEAD CALCIUM TITANATE

Substitutional aspects is an area of great interest from the view point of fundamental studies on the properties of ferroelectrics as well as for a variety of applications. Several combinations of the lead titanate series in the form of solid solutions have been investigated for the purpose of obtaining improved physical properties. In recent years, modified lead titanate ceramics have been developed which possess extremely anisotropic piezoelectric properties. These materials include compounds of (Pb$_{(1-x)}$A$_{x}$)(Ti$_{(1-y)}$B$_{y}$)O$_{3}$, where a number of both isovalent and off-valence substitutions for both Pb(A-site) and Ti(B-site) are possible. Lead can be substituted by covalent cations including Ca$^{2+}$, Ba$^{2+}$, Sr$^{2+}$ and Cd$^{2+}$ as well as off-valence substitutions such as rare-earth ions Sm$^{3+}$ and Y$^{3+}$ while maintaining the perovskite crystal structure responsible for the strong ferroelectric behaviour (Rittenmyer and Ting 1990).

The transducer characteristics of the piezoelectric material can be carefully tailored because of the many possible variations in crystal chemistry but, at present, lead titanate ceramics modified with samarium and calcium are found to possess the highest piezoelectric anisotropy. The properties of PbTiO$_{3}$ are known to be varied by the addition of calcium (Ganesh and Goo 1997). The substitution of Ca is found to alter the transition temperature and also decreases the c/a ratio. The Pb$_{1-x}$Ca$_{x}$TiO$_{3}$ solid solutions are the base of many reactive materials with high anisotropy in piezoelectric properties. In recent years the use of calcium modified PbTiO$_{3}$ ceramics (Yamashita et al 1984; Del Olmo 1988; Jimenez et al 1988; King et al 1988;
Eremkin et al 1994; Ichinose and Komachi 1994) were tried with success as an alternative material to PZT ceramics (Clarke and Whatmore 1976; Yamamoto 1996).

Ferroelectric ceramics of PbTiO$_3$ modified with Ca have been gaining interest in the area of ultrasonic piezoelectric transducers due to the absence of lateral vibrational modes (Mendiola et al 1988). A low mechanical quality factor and a large electromechanical anisotropy are the most important factors to make high frequency ultrasonic ceramic transducers for use in echography. However the reliable values of various physical property of the material cannot be derived from the ceramics, since the properties are modified by preparatory conditions.

5.4.1 Crystal growth - survey

In the growth of PCT crystals, several factors must be taken into consideration. Lead containing oxides with the perovskite structure and their solid solutions used for the synthesis of PCT crystals melt incongruently. Further difficulties are the volatility and reactivity of PbO at high temperatures. The flux method of crystal growth offers the possibility of growth at reasonably low temperatures. The first attempt on the crystal growth in the Pb$_{1-x}$Ca$_x$TiO$_3$ system has been reported by Ichinose and Komachi (1994) using PbO as a flux. The grown crystals show no considerable variation in the Curie temperature with Ca content and it is tetragonal at room temperature upto 50 mol.% of Ca.

Eremkin et al (1994) have grown PCT crystals using PbO-B$_2$O$_3$ flux and constructed the phase diagram from the optical measurement data obtained during heating mode (Figure 5.6). The ferroelectric phase transition temperature decreases with Ca upto 50 mol.% and the tetragonal phase transforms to orthorhombic structure. According to their data the boundary between the tetragonal and orthorhombic ferroelectric phases is located at 42 mol.% of Ca at room temperature.
Figure 5.6 Phase diagram of PbTiO$_3$-CaTiO$_3$ system
(Eremkin et al 1994)

Phases I, II, IV - Tetragonal
II - Cubic
V, VI - Orthorhombic
I, IV & V - Ferroelectric
Attempts to grow these crystals using KF flux by Remeika’s technique (1954) yielded crystals black in colour and a few thin crystals were transparent (Balakumar et al. 1998). A decrease in the tetragonality was observed with increasing Ca content.

In the present work crystal growth of Pb$_{1-x}$Ca$_x$TiO$_3$ ($x=0, 0.05, 0.1$) has been carried out from PbO flux to obtain single crystals suitable for X-ray, DSC and domain property studies.

5.5  EXPERIMENT
5.5.1  Growth of BaTiO$_3$ crystals

Barium titanate crystals were grown by Remeika’s technique in a cylindrical muffle furnace heated with Al Kanthal wire. The furnace was fabricated such that there was no gradient at the position of the crucible. The composition of the starting materials was 10 mol.% of BaTiO$_3$ and 90 mol.% of KF. The BaCO$_3$ and TiO$_2$ was added in proper proportions to give BaTiO$_3$. In each growth run 15g of BaTiO$_3$ was added at the bottom of the platinum crucible (volume 50cc) with the KF (34g) covering it at the top. The chemicals were Aldrich make and 99.99% pure. Since KF is less dense all the charge cannot be loaded into the crucible in a single step. Hence a two step process was followed. Initially 20g of KF was added to the charge and then the crucible was downloaded into a preheated furnace kept at 1000°C. After a few minutes the crucible was taken out. Now there will be enough volume in the crucible since KF melts completely at this temperature. As a second step the remaining KF was loaded into the crucible. The crucible containing this charge was tightly covered with a platinum lid and placed directly into the furnace held at the soaking temperature of 1100°C. The furnace was held at this temperature for 5 hours and then cooled at the rate of 17°C/h till 900°C using an Eurotherm 818P controller. Then the charge was cooled at the rate of 40°C/h till room temperature.
5.5.2 Growth of PbTiO₃ crystals

The raw materials used for the growth PbTiO₃ crystals were of high purity Aldrich PbO (99.9%) and TiO₂ (99.99%). All compositions were prepared in accordance with the formula (1-x)PbO+xTiO₂ with x varying from 20-30 mol%. High gradient vertical type SiC furnace with Eurotherm temperature controller (818P) and 100cc platinum crucible were employed. After loading the charge into the platinum crucible it was covered with a flat platinum lid to avoid evaporation of the flux. The crucible was placed inside the furnace supported by a refractory brick. With rapid heating from room temperature (200°C/h) initial homogenization was done at 1150°C for 10 hours. Then the furnace was cooled at a rate of 15°C/h till 900°C. After this crystal growth regime the temperature was lowered at a faster rate of 30-40°C/h till 525°C. Since the c/a ratio is very large, a slow cooling rate of 2-5°C/h was adopted when it reached the phase transition temperature (around 490°C). Hot acetic acid was used to separate the crystals from the solidified flux. Yellowish, transparent PbTiO₃ single crystals were harvested from the flux.

5.5.3 Growth of Pb₁₋ₓCaₓTiO₃ crystals

For the growth of Pb₁₋ₓCaₓTiO₃ crystals the stoichiometric compositions of each batch (x=0.05, 0.1) comprising Aldrich make PbO(99.9%), CaCO₃(99.99%) and TiO₂(99.99%) was accurately weighed and ground in a mortar for 1 hour and calcinated around 900°C. This was again well mixed in mortar and then loaded into a platinum crucible of volume 100cc along with the required proportion of PbO. The crucible was closed with a tight fitting platinum lid to avoid PbO evaporation. The furnace was fired to 1150°C and soaked for 10-12hours. After sufficient homogenization cooling was commenced at the rate of 1-4°C/h. After reaching 525°C a very slow cooling rate of 1-2°C/h is adopted till 350°C in order to reduce the
thermal stress around the transition temperature. The crystals were separated from the solidified flux using hot acetic acid or 1:8 ratio of HNO₃ and H₂O.

5.6 RESULTS AND DISCUSSION

5.6.1 Barium titanate

The process of direct loading of the charge at the temperature of 1100°C is favoured to get a considerable quantity of barium titanate in the solution and to avoid the evaporation of KF (Bradt and Ansell 1967). The crystals which resulted from the standard Remeika’s technique were generally found in the crucible as shown in Figure 5.7a. The best results were obtained when cake formation covered the crucible bottom. This cake formation is a coarse yellow powder of 5mm thickness.

The volatilization of KF is appreciable above 1000°C and as a result the solution particularly at the surface becomes supersaturated more rapidly. During the soaking period the total composition changes isothermally towards BaTiO₃ and during this period the cake formation occurs (DeVries 1959). Over the temperature range from 1050-1000°C, the butterfly twins and accompanying dendritic forms generally grew into the solution from both the bottom and sides of the crucible and moved upward from the cake.

Two different habits of crystal growth were observed in these experiments. A mass of chunky crystals was usually found on the bottom of the crucible. Growing out of this layer were large number of thin plates, always in pairs as butterfly wings. They protrude upwards from the melt as shown in Figure 5.7a. The crystal plates (Figure 5.7b) were separated from the flux by soaking the crucible in hot water by dissolving the fluoride rapidly. The twins were very fragile and easily breakable along the length of the spine.
A - SMALL CRYSTALS
B - BUTTERFLY TWIN AND DENDRITE ZONE

Figure 5.7a  Schematic representation of KF-grown BaTiO$_3$ crystals in the crucible

Figure 5.7b  Single crystals of BaTiO$_3$

Figure 5.7c  Schematic representation of twinning in BaTiO$_3$
This twin is known to be a double (111) twin having the appearance of two isosceles right angle triangles with a common hypotenuse (Figure 5.7c). The large planes of the triangles are (100) planes as the backbone of the twin (Nielsen et al 1962). One type of butterfly wing is an obtuse 109° angle crystal that contains a single (111) twin between two (100) planes; while the other is an acute 30° angle crystal that has two (111) twins between the (100) planes (White 1955). This twin formation is due to the occurrence of hexagonal phase stacking fault during the starting of the nucleation (DeVries 1959). This platelike growth habit of barium titanate "butterfly" twins represents a consistent deviation from the more equivalent morphology expected for a cubic crystal. This special habit does not get affected by purity of chemicals, cooling rate and crucible shape (DeVries 1959).

5.6.2 Lead titanate

PbTiO₃ crystals grew mainly in the form of cubes and thick plates. Most of the crystals settled at the bottom and a few were found to be sticking to the walls of the crucible. The large size crystals grew in the center of the crucible. The vertical gradient in the furnace was about 10°C/cm. The temperature near the bottom of the crucible being higher ensures vertical convection flow of the solution favouring the crystal growth. The yield of perfect crystals also depends on the ratio between the temperature gradient over the height of the melt and the cooling rate (Fesenko et al 1972). Results of various flux charge ratio used for the growth of PbTiO₃ crystals are given is Table 5.1. Repeated growth runs were performed for the composition 75mol% of PbO and 25 mol% of TiO₂ which was found to give better results. A soaking temperature of 10hours is required for complete dissolution of TiO₂. Otherwise undissolved TiO₂ particles will act as nucleation centers, which might dramatically reduce the size of the grown crystals.

The crystals were thick platelets with dimensions 2x1.2x0.3cm³ (Figure 5.8a), the largest face being (001) (Ganesa Moorthy et al 1998a). Large crystals have flux
Table 5.1

Results of various flux ratios for pure PbTiO$_3$ crystals

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>PbO:TiO$_2$ mol.%</th>
<th>Crystallization range, °C</th>
<th>Soaking hours/cooling rate</th>
<th>Colouration</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>70:30</td>
<td>1150-900</td>
<td>10h, 15°C/h</td>
<td>Light yellow</td>
<td>One large size and a few tiny crystals</td>
</tr>
<tr>
<td>2</td>
<td>75:25</td>
<td>1150-900</td>
<td>10h, 15°C/h</td>
<td>Yellow</td>
<td>One large size crystal (2x1.5x0.3cm$^3$) with several crystals of dimension 4x4x2mm$^3$</td>
</tr>
<tr>
<td>3</td>
<td>80:20</td>
<td>1150-900</td>
<td>10h, 15°C/h</td>
<td>Dark brown or nearly black</td>
<td>Large crystals but they are heavily twinned</td>
</tr>
</tbody>
</table>
Figure 5.8  Single crystals of PbTiO$_3$ obtained under various growth conditions
inclusions on the surface which can be eliminated by lapping. If the soaking period is reduced, there were lot of inclusions in the crystal affecting the transparency even though the size and position where the crystal nucleates in the crucible are the same (Figure 5.8b). The same observation was found even while increasing the TiO₂ content in the melt. If the content of TiO₂ exceeds 30 mol.% mostly crystals end up with black colour independent of the cooling rate and soaking period (Figure 5.8c).

A few best PbTiO₃ (Figure 5.8d) crystals could be separated from upper conglomerate of the crucible for the 75:25 mol.% ratio. These crystals were used for the domain studies. These were the crystals obtained by adopting a very slow cooling rate around the phase transition temperature. Alternatively when the furnace was switched off after growth, allowing a fast cooling around the ferroelectric transition temperature, most of the crystals get cracked (Figure 5.8e). This is due to the large c/a ratio around the transition temperature (490°C) and the strain caused due to fast cooling. These crystals were heavily twinned and the macro domains formed due to the strain could be easily seen even with naked eye.

5.6.3 Lead calcium titanate

A sufficient holding time at a constant temperature is required to dissolve TiO₂ and CaCO₃ for the growth of PbCaTiO₃ crystals during cooling. Since the melting point of CaTiO₃ (1915°C) is higher than that of PbTiO₃ (1285°C) the holding temperature for the PbₓCaₓTiO₃ system is higher. As this holding time increases beyond 10-12 hours, black colouration results in the crystals. The solute/solvent ratio was varied with respect to the calcium concentration nominally increasing for more percentage of calcium.

Figure 5.9a shows the crystals grown for 5 mol.% of calcium. These crystals were obtained for a cooling rate of 2°C/h. The size of the crystals was limited by the flux ratio and the cooling rates. Solubility of the solute decreases with increase of Ca
Figure 5.9 Single crystals of Pb$_{1-x}$Ca$_x$TiO$_3$
content. Hence, the flux ratio was increased for higher Ca content. After several growth runs the flux ratio was optimized in order to grow equidimensional crystals for each composition which are tabulated (Table 5.2). Figure 5.9b shows the crystals for 10 mol.% of calcium. For all the compositions, the crystals were found over the entire volume of the crucible. However, crystals found at the center of the crucible were larger in size compared to those near the crucible walls. It has been possible to grow single crystals of dimensions 3x3x2mm³. If the cooling rate is increased to 5°C/h tiny crystals of dimension 1-2mm³ were obtained as shown in the bulk mass for Pb₀.₉⁵Ca₀.₀₅TiO₃ (Figure 5.9c). Even though these crystals were transparent their separation from the flux is very difficult.

5.7 CHARACTERIZATION

5.7.1 Surface morphology

The surface morphology of the crystals depends upon the cooling rate (Bhide et al 1968; Balakumar et al 1995). Dendrites were observed for higher supersaturation. The dendritic pattern is having vein like structure. Figure 5.10a and Figure 5.10b shows the vein like structure on the surface of BaTiO₃ and Pb₀.₉⁵Ca₀.₀₅TiO₃ single crystals. This is caused by growth instability due to very high cooling rate. The origin of dendritic patterns is associated with high supersaturation. Supersaturation decreases as the growth progresses and hence regions between dendritic arms were filled up at this stage and the growth of flat and smooth crystals finally proceeds by the layer growth mechanism which favours the growth of platelets.

The surface studies on the as-grown faces of single crystals obtained under conditions of low and constant supersaturation, reveal that in a large number of cases they are perfectly flat without any growth features. The surfaces of the grown crystals are shiny. PbTiO₃ crystals were rectangular or cubic in shape, with domain walls penetrating. When the crystals were cooled very slowly through the transition
Table 5.2

Experimental details and results of single crystal growth of Pb$_{1-x}$Ca$_x$TiO$_3$

<table>
<thead>
<tr>
<th>Starting Composition</th>
<th>Solute/Solvent PCT: PbO ratio Mol%</th>
<th>Temperature range °C</th>
<th>Soaking/Cooling Hours/ rate</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbTiO$_3$</td>
<td>25:75</td>
<td>1150-950</td>
<td>10h, 4°C/h</td>
<td>4x4x2mm$^3$</td>
</tr>
<tr>
<td>Pb$<em>{0.95}$Ca$</em>{0.05}$TiO$_3$</td>
<td>23:77</td>
<td>1150-950</td>
<td>10h, 2°C/h</td>
<td>4x4x1mm$^3$ and several small crystals</td>
</tr>
<tr>
<td>Pb$<em>{0.9}$Ca$</em>{0.1}$TiO$_3$</td>
<td>20:80</td>
<td>1150-950</td>
<td>12h, 2°C/h</td>
<td>3x2x1mm$^3$</td>
</tr>
</tbody>
</table>
Figure 5.10  Vein like structure on the surface of
(a) BaTiO$_3$ and (b) Pb$_{0.95}$Ca$_{0.05}$TiO$_3$ crystals

Figure 5.11 Two-dimensional layer growth observed on
(a) PbTiO$_3$ crystals by optical microscope and
(b) Pb$_{0.9}$Ca$_{0.1}$TiO$_3$ crystals by AFM
temperature, it is found that the crystals are free from surface twinning and growth striations, showing good homogeneity.

On the (001) face of the as-grown crystals of PbTiO$_3$, bunch of layers was observed and some microflux inclusions were also seen. The distance between steps were larger when they approached the edge of the crystals. They revealed that the crystal grows layer by layer with a 2D mechanism. Figure 5.11a shows the layer growth mechanism observed on the as-grown crystals of pure PbTiO$_3$ (Ganesa Moorthy et al 1998a). Figure 5.11b shows the layers observed on the surface of lead calcium titanate single crystal by atomic force microscopy.

5.7.2 X-ray analysis

Powder diffraction patterns were recorded by using Rich Seifert X-ray diffractometer with CuK$_\alpha$ ($\lambda=1.5418\text{Å}$) radiation. Figure 5.12 shows the powder X-ray diffraction pattern of crushed crystals of BaTiO$_3$ which reveals that the grown crystals possess tetragonal structure with lattice parameter values $a=3.9931\text{Å}$ and $c=4.0365\text{Å}$.

Figure 5.13 depicts the X-ray powder diffraction pattern of PbTiO$_3$ and Pb$_{1-x}$Ca$_x$TiO$_3$ ($x=0.05$ and $0.1$). X-ray analysis confirmed the crystalline nature and indicated that there is no significant separation of TiO$_2$, CaCO$_3$ and PbO. The diffraction studies revealed that the room temperature structure is tetragonal. Close observation of the peak position and d-spacing confirmed that the tetragonality at room temperature decreases with increase in Ca content. The $a$ and $c$ parameters are in good agreement with values in the literature (Balakumar et al 1998; Ganesa Moorthy et al 1998a; 1998c). The variation in $a$ and $c$ parameters was calculated by least square fitting method using Bragg's law. The decrease of $c/a$ ratio confirms the decrease of tetragonality with increase of Ca (Table 5.3) and is in agreement with the reported values (Eremkin et al 1994; Balakumar et al 1998).
Figure 5.12  X-ray powder diffractogram of BaTiO$_3$
Figure 5.13  X-ray powder diffractogram of (a) PbTiO₃, (b) Pb₀·₉₅Ca₀·₀₅TiO₃ and (c) Pb₀·₉Ca₀·₁TiO₃
### Table 5.3

**Lattice parameters of PbTiO₃ and PbCaTiO₃ single crystals**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Lattice parameters</th>
<th>Volume (Å³)</th>
<th>c/a ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a (Å)</td>
<td>c (Å)</td>
<td></td>
</tr>
<tr>
<td>PbTiO₃</td>
<td>3.901</td>
<td>4.148</td>
<td>63.1234</td>
</tr>
<tr>
<td>Pb₀.₉₅Ca₀.₀₅TiO₃</td>
<td>3.904</td>
<td>4.132</td>
<td>62.9767</td>
</tr>
<tr>
<td>Pb₀.₉Ca₀.₁TiO₃</td>
<td>3.910</td>
<td>4.117</td>
<td>62.9411</td>
</tr>
</tbody>
</table>
Figure 5.14 DSC spectra of (1) PbTiO₃ and (2) Pb₀.₉₅Ca₀.₀₅TiO₃ crystals
5.7.3 Differential scanning calorimetry

To study the high temperature ferroelectric phase transformation, differential scanning calorimetry was performed and measured during heating at a rate of 10°C/min. An endothermic peak was observed at 496°C for pure PbTiO$_3$ and at 467°C for Pb$_{0.95}$Ca$_{0.05}$TiO$_3$ (Figure 5.14). It is evident from the second curve that the substitution of Ca affects the transition temperature and found to decrease with Ca incorporation. Combining DSC results with the powder diffraction results, it is confirmed that the cubic to tetragonal transition shifts towards lower temperature side with the increase in Ca content which are consistent with reported values (Eremkin et al 1994; Balakumar et al 1998).

5.8 CONCLUSION

BaTiO$_3$ crystals were grown from KF flux by Remeika's technique with a slight modification in a gradient free furnace. A low soaking period and high cooling rate favoured the growth of butterfly twins.

A high gradient furnace was found to improve the growth of PbTiO$_3$ and Pb$_{1-x}$Ca$_x$TiO$_3$ (x=0.05, 0.1) single crystals from high temperature solution. Ferroelectric lead titanate crystals of dimension 2x1.2x0.3cm$^3$ were grown using self flux. The lattice parameters of the grown crystals confirmed the tetragonal nature at room temperature. X-ray powder diffraction analysis confirmed the decrease in tetragonality with increasing Ca content in PbCaTiO$_3$ crystals. Growth layers observed on the crystals indicate a two dimensional layer growth mechanism. The measured Curie temperature for tetragonal-cubic phase transformation using Differential Scanning Calorimetry is 490°C for x=0 and 467°C for x=0.05 depending on the Ca concentration.