Chapter 3

Processing of Key Pyroelectric Materials

3.1 Introduction

Pyroelectric materials have been fabricated in bulk single crystals, ceramic (polycrystalline), films, and composite forms. This chapter briefly reviews and describes all of the major and relevant techniques for processing key materials.

3.2 Bulk Single Crystals

The growth of bulk single crystals, although simple in principle, requires meticulous attention to detail. Knowledge of the phase diagram for both the constituents of the crystals and any solvent involved is essential. The mechanical and electrical equipment involved must be able to ensure uniform conditions over the extended growth period required to cultivate a single crystal of any size. Furthermore, apparati must mitigate excessive vibrations and thermal disturbances.

3.2.1 Growth of crystals from solution

Highly homogeneous crystals can be grown by slow cooling saturated solutions of chosen materials or, sometimes, by the slow evaporation of a solution at a constant temperature. The growth of crystals from solution at low temperatures occupies an important place in the area of crystal growth techniques, especially because materials are not stable at elevated temperatures.

A number of concepts for solution-crystal growth systems are found in the literature.[1] One of the best methods for growth of both inorganic and organic crystals from solution is to slowly lower the temperature of a solution, provided the material has a positive temperature coefficient of solubility. In this method, a saturated solution of the material is prepared in an appropriate solvent at a chosen temperature and kept at this temperature for 24 h. The seed-holding rod is then inserted into the growth chamber, after which it is rotated. The growth process is enacted by lowering the temperature slowly at

a preprogrammed rate, typically 0.05–2.0 °C per day, depending on the solubility of the chosen material. The complete crystallization process may take from one to several weeks. To terminate the growth process, the grown crystals are taken out of the solution without incurring thermal shock. Conditions for this solution-growth method must include the proper solvent of the pyroelectric material with a positive temperature coefficient of solubility. Large pyroelectric crystals, made with such materials as triglycine sulfate (TGS) and potassium dihydrogen phosphate (KDP), have been successfully grown using the solution-growth method. Single crystals of TGS are usually grown from an aqueous solution through either the temperature-lowering or solvent-evaporation method. The authors have successfully grown large TGS crystals using the crystallizer illustrated and described in Ref. 1. The major components of a typical crystallizer designed by the authors are shown in Fig. 3.1.

Several advancements in crystallizer designs and techniques have made growing TGS crystals more efficient.[2–5] Brezina et al. designed a crystallizer for growing L-alanine-doped deuterated triglycine sulfate (DLATGS) crystals by isothermal evaporation of D_2O.[2] Satapathy et al. have described a novel technique for mounting the TGS seeds and a crystallizer.[3] Banan has also described seed holders and a crystallizer for growing pure and doped TGS crystals.[4] TGS crystals weighing more than 100 grams have been grown from solution with ethyl alcohol additions.[5] When alcohol is mixed in an aqueous solution of TGS, a portion of the water in the solution associates with the alcohol, concentrating the solution. Thus, the supersaturation can be controlled to a certain degree, making it easier to grow TGS crystals. To achieve success when growing crystals from aqueous solutions, it is important to prepare a solution with a carefully determined saturation temperature and solubility profile, and to ensure the absence of any foreign particles.

3.2.2 Crystal growth from melt

The Czochralski crystal-growth technique is illustrated in Fig. 3.2 with the various components labeled.[6] To qualify for crystal growth using the Czochralski technique, the material should have a relatively low vapor pressure. The crucible material should be nonreactive with the crystal-growth material above its melting point. The Czochralski system is based on the following procedure: (1) the material is melted in a crucible and kept for few hours at a temperature above the melting point, (2) the temperature is then reduced to a value slightly above the freezing point, which is determined by cooling the melt until crystals begin appearing on the surface, (3) the temperature is slightly lowered, and a seed (cut in the appropriate orientation) is inserted into the melt and kept in that position for a half an hour or so, (4) the pulling mechanism of the seed is initiated, (5) if the temperatures have been chosen correctly (based on the material used), the seed should form the
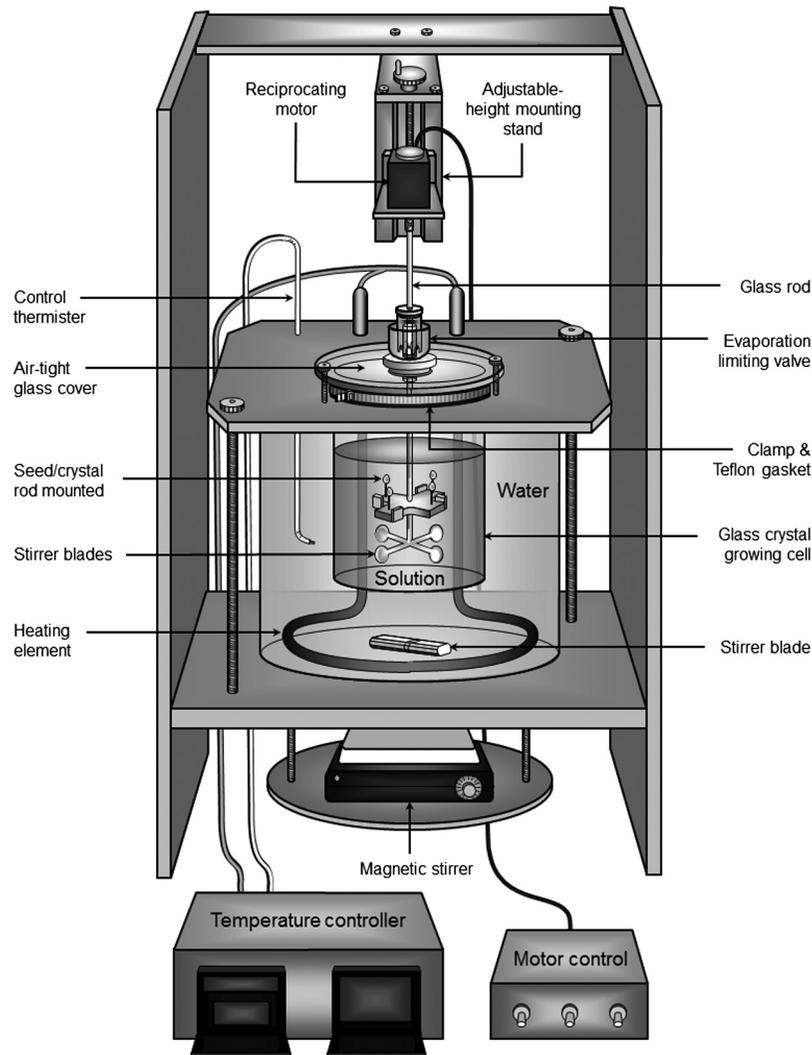
Figure 3.1 A solution-growth crystallizer designed and fabricated at AAMU.[1]

crystallization center. If the crystal grows very fast and becomes visible to the naked eye, increase the temperature of the melt by a degree or so. This must be done carefully because if the melt is overheated, the crystal will dissolve and separate from the melt. The diameter of the pulled crystal is controlled by manipulating both the melt temperature and the pulling rate. Suitable thermal engineering of both axial and radial temperature gradients is needed to reliably grow single crystals of desired dimensions. Pyroelectric single crystals of lithium tantalate, lithium niobate, potassium tantalate niobate, and others have been successfully grown using the Czochralski method.[7]
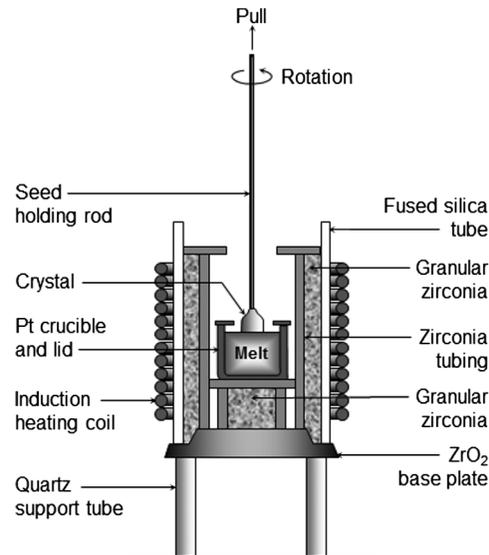
Figure 3.2   Schematic diagram of Czochralski crystal growth technique.

3.3 Preparation of Ceramics

Ceramic oxide compositions can generally be produced by thoroughly mixing the constituents as oxides or compounds (such as carbonates and nitrates), which readily decompose into oxides and calcines at the correct (material-specific) temperature, giving substantial interdiffusion of the cations. The calcine is then ground and compressed into the desired shape and sintered at a temperature a few hundred degrees above the calcination temperature.[8] For example, for the calcination of lead zirconate titanate [PZT: $Pb(Zr, Ti)O_3$], the raw materials PbO, TiO_2, and ZrO_2 are mixed in the molar ratio of 2:1:1, pressed into lumps, and then calcined in ambient air at 800°C to obtain the perovskite phase. The calcination temperature is of great value as it influences the density and, hence, the electromechanical properties of the final product. However, calcining PZT at $T > 800\,°C$ could cause lead (Pb) loss, resulting in detrimental effects on the electrical properties. Calcination at the appropriate temperature is, therefore, necessary to obtain the best electrical and mechanical properties. After calcining, the lumps are ground by milling. The green bodies should have a material-specific minimum density before they can be sintered. The desired shape and minimum green density can be achieved through various techniques including powder compaction, slip casting, and extrusion.

   The choice of method depends on several factors, including the type of powder used, the particle size distribution, the state of agglomeration, the desired shape, and the thickness of the part. After shaping, the green bodies are
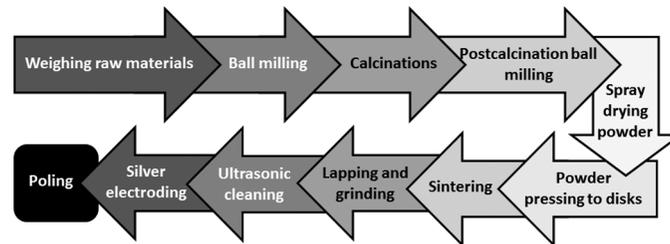
Figure 3.3 Flowchart of fabrication and processing of ferroelectric ceramics.

heated slowly to between 500 and 600 °C to remove any binder present. The binder burnout rate should be $\leq$ 1–2 °C/min in order to allow the gasses to exit slowly without forming cracks and blisters in the ceramic pieces. After the binder burnout is complete, the samples are raised to a higher temperature for sintering. The sintering temperature and time must be optimum to allow for proper densification without abnormal grain growth. The sintering of oxide ceramics must be carried out in an oxidizing atmosphere or in air. For ceramics containing lead (such as PZT, PT, PLZT, etc.), lead loss occurs at temperatures above 800 °C. In order to reduce lead loss during sintering, samples must be kept on a sealed crucible containing saturated vapor. Figure 3.3 is a flowchart showing the fabrication of ceramics and sample preparation for characterization.

3.4 Thin-Film Deposition

The fabrication of ferroelectrics began with simple thermal evaporation of $BaTiO_3$ by Feldman in 1955.[9] Since then, a number of deposition techniques have been developed. The various techniques can be classified into two categories: solution deposition and nonsolution deposition. This section provides a brief review of techniques for the fabrication of PZT films.

3.4.1 Nonsolution deposition

3.4.1.1 Sputtering technique

The convenience and high melting point of PZT materials used in sputtering methods [DC, RF magnetron, electron cyclotron resonance (ECR) magnetron, and ion beam], make it the most widely used technique for fabricating ferroelectric thin films.[10] During the sputtering process, the material is set as a sputtering target, serving as the cathode in the electric circuit. The substrates are placed on a grounded anode and positioned at a predetermined distance from the target. The target might consist of a series of individual elements aligned on a rotatable stage or a ceramic target that contains the required compositions.