Chapter 3

Experimental Work

This chapter focuses on (i) the synthesis of CCTO and Nb, Sn, Zr doped CCTO by solid state method, (ii) synthesis of La doped CCTO by semi wet method (ii) preparation of CCTO and La, Nb, Sn, Zr doped CCTO dispersed PVDF composites by extrusion method, (iii) details of different characterization techniques such as XRD, SEM, TGA, Tensile test and measurement and analysis of dielectric properties.

3.1 Ceramic Preparation:

$CaCu_3Ti_4O_{12}$ (CCTO), $CaCu_3Ti_{4-5x/4}Nb_xO_{12}$ (NbCCTO) with x=0.05, $CaCu_3Ti_{4-x}Sn_xO_{12}$ (SnCCTO) with (x=0.05) and $CaCu_3Ti_{4-x}Zr_xO_{12}$ (CCTZO) with x=0.10 have been synthesized by conventional solid state technique. Powders of $CaCO_3$ (99.98%), CuO (99.5%), TiO_2 (99.55%), Nb_2O_5 (99.98%), SnO_2 (99.98%) and ZrO_2 (99.98%) taken in stoichiometric amount are mixed and ground for 12 hours. These are calcined in air at 1000^0 C for 12 hours with intermittent grinding. Formation of the single phase solid solution is confirmed by powder X-ray diffraction (XRD) using CuKα radiation. Calcined powders are ground and mixed with 2% PVA (Molecular weight 37000) solution to make pellets of 15 mm diameter and 2 mm thickness under a load of 6 tons using a hydraulic press. The pressed pellets were sintered at 1000^0C for 6 hours. Sintered pellets were again ground to make fine powder using an agate mortar and pestle.

A semi-wet route has been used to synthesize samples of $Ca_{(1-3x/2)}La_xCu_3Ti_4O_{12}$ (x= 0.05). Analytical grade, $Ca(NO_3)_2$.$4H_2O$, $La(NO_3)_3$.$6H_2O$, $Cu(NO_3)_2$.$3H_2O$, TiO_2 and citric acid having purity better than 99.95% have been used as starting materials. Solutions of the metal nitrates of these metallic ions in stoichiometric amount are mixed in a beaker. Calculated amount of TiO_2 and citric acid equivalent to the metal ions are added to the above solution. The mixture is heated at 70–80° C on a hot plate to evaporate water and then dried at 100–120°C in a hot air oven for 12 h to yield a blue powder. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of the powder have been done from 30 to 1000°C at a heating rate of

10°C/min in air using Perkin-Elmer, USA TGA/DTA Analyzer. Calcination has been done at 800°C in an electrical furnace for 6h. Pellets of the well mixed calcined powder are made using a hydraulic press and sintered at 900°C for 6h. X ray diffraction patterns of the sintered pellets confirm the formation of single phase solid solution.

3.2 Composite preparation:

Poly (vinylidene fluoride) (PVDF), (SOLEF 6008; Ausimont, Italy) with a melt flow index of 24 g/10 min at 230^{o}C under 5 kg load was used in this work. Melt extrusion process was used for the fabrication of PVDF/CCTO and doped CCTO composites. In this method, 12 gms of the polymer was mixed with 10, 20 and 50 wt% of ceramics (CCTO, LaCCTO, NbCCTO, SnCCTO and CCTZO) in a high speed mixer for 20 min before putting it into the extruder. Extrusion was carried out in a twin-screw extruder (Hakke Mini Lab) (Fig 3.1). Mixing was done at 205°C for ~10 minutes under a speed of 70 rpm. The polymer chains mix uniformly with ceramic particles during melt mixing. PVDF and composites were melt-pressed into thin films of 100 μm thickness in a compression-molding machine at 190°C under a load of 5 tons.

Figure 3.1 Twin-screw extruder (Hakke Mini Lab)

Table 3.1 List of raw materials used in the synthesis of these systems is given below.

S. No.	Materials Used	Chemical Formula	Purity	Manufacturer
1.	**Calcium Carbonate**	$CaCO_3$	99.98%	Sigma Aldrich
2.	**Lanthanum nitrate hexahydrate**	$La(NO_3)_3.6H_2O$	99.95%	Sigma Aldrich
3.	**Copper(II) oxide**	CuO	99.5%	Sigma Aldrich
4.	**Titanium dioxide**	TiO_2	99.55%	Sigma Aldrich
5.	**Niobium Pentoxide**	Nb_2O_5	99.98%	Sigma Aldrich
6.	**Tin dioxide**	SnO_2	99.98%	Sigma Aldrich
7.	**Zirconium dioxide**	ZrO_2	99.98%	Sigma Aldrich
8.	**Poly(vinylidene fluoride)**	PVDF	-----	SOLEF 6008; Ausimont, Italy

3.3 Characterization:

3.3.1 X-ray diffraction

X-ray diffraction (XRD) patterns are recorded using Rigaku Desktop Miniflex II X-Ray diffractometer employing Cu-Kα radiation and Ni-filter (wavelength, λ= 0.15418 nm) (Fig 3.2). Films (~100 μm thickness) of PVDF and the composites are scanned in the diffraction angle, 2θ range 10° - 90° at a scan rate of 3°/min.

Figure 3.2 Rigaku Desktop Miniflex II X-Ray diffractometer

3.3.2 Scanning Electron Microscopy

SEM images have been recorded using INSPECT S 50 FP 2017/12 Scanning Electron Microscope (Fig 3.3). Gold is coated by sputtering on one plane surface of the samples to make it conducting.

Figure 3.3 INSPECT S 50 FP 2017/12 Scanning Electron Microscope

3.3.3 Thermal analysis

Thermogravimetric analysis (TGA) of PVDF and its composites was carried out in the temperature range 30-700°C at a heating rate of 10°C/min in air using TGA/DTA Analyser, Perkin-Elmer, USA (Fig 3.4). A few milligrams of the test sample and an inert reference sample, Al_2O_3 powder were placed in two alumina crucibles and put side by side in a heating block.

Figure 3.4 TGA/DTA Analyser, Perkin-Elmer, USA (www.perkin-elmer.com).

3.3.4 Mechanical Properties

For measurement of mechanical properties, samples are prepared by using injection molding technique (Microinjector, Model FD-1, Fly Tech Engineering) (Fig 3.5 a). Temperature of the mould was maintained at 60°C and that of the cylinder at 210°C under a pressure of 100 bars. The sample prepared by this method has cross sectional dimensions of 2.15 X 4 mm^2, the length of the gauge section was kept 20 mm. Tensile tests are performed on the microinjected dog bone shaped samples at room temperature using Instron 3369 tensile machine (Fig 3.5 b). A constant crosshead speed of 5 mm/min is selected and the stress–strain data are recorded up to the complete breaking of the samples. Three samples are tested for each composition.

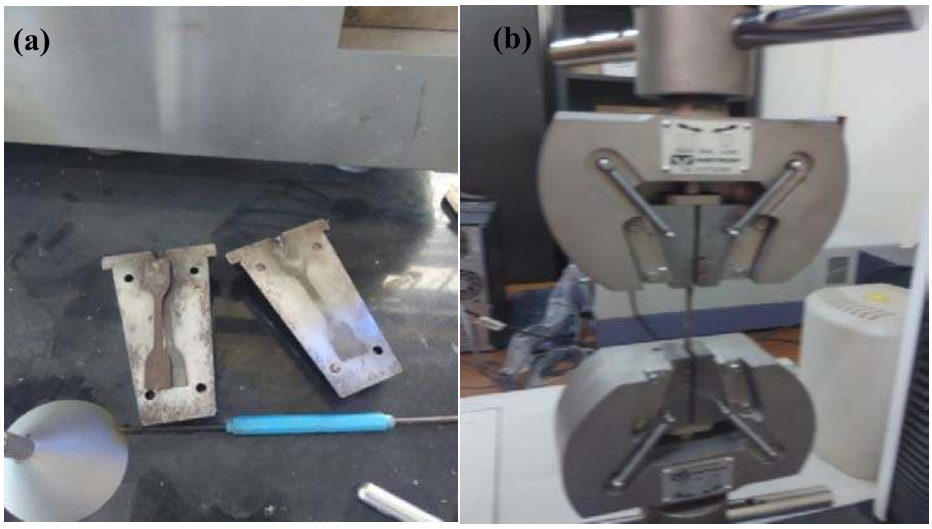

Figure 3.5 (a) Tensile test specimen (b) Instron 3369 tensile machine

3.3.5 Dielectric measurements

Dielectric properties are measured on the disc-shaped films of 12 mm diameter. These are coated with silver and measurements are made in the frequency range 10^{-2}-10^{6} Hz using Novocontrol (Alpha-A High Performance Analyzer ZG4) from room temperature to 120°C at a few steady temperatures viz 40^{0}C, 60^{0}C, 80^{0}C, 100^{0}C and 120^{0}C (Fig 3.6). Temperature-dependent dielectric relaxation has also been explained by Havriliak-Negami (H-N) function using Win fit software.

Figure 3.6 Novocontrol (Alpha-A High Performance Analyzer ZG4)