
EXPERIMENTAL METHODS

3.1 Material Synthesis**3.1.1 Raw materials**

The raw materials having purity more than 99%, were obtained from various manufacturers. Table 3.1 below enlists the chemicals used, their purity level and the names of manufacturers. The fine chemicals used here are mainly in the form of oxides and carbonates.

Table 3.1 The list of raw materials with percentage purity and names of manufacturers.

S. No.	Name of Chemical	Purity (%)	Manufacturer
1	BaCO ₃	> 99	Thomas Baker
2	SrCO ₃	> 99	Thomas Baker
3	TiO ₂	> 99	Loba Chemie
4	PbO	99.9	Malinckrodt Inc.
5	H ₃ BO ₃	99.5	Thomas Baker
6	SiO ₂ (Quartz)	99.9	HiMedia
7	Bi ₂ O ₃	99	Alfa Aesar

3.1.2 Preparation of BST ceramics

The high purity raw materials i.e. BaCO₃, SrCO₃ and TiO₂ were used for preparation of Ba_{0.5}Sr_{0.5}TiO₃ (BST). The BST ceramic was prepared by conventional solid-state route. The raw materials were weighed in stoichiometric proportion (described in Table 3.2) and mixed thoroughly in ball mill at 50 rpm for 24 h using yttria stabilized zirconia balls and acetone as grinding media. The mixed slurry was dried in oven at 333K for 2 h. The obtained powder was kept in an alumina crucible for calcination at 1273K for 4 h with the heating and cooling rate of 5 K/min in PID controlled electric furnace. Calcined powder

was then ground well to reduce the lumps into fine powder and then passed through 200 mesh size sieve.

Table 3.2 Calculation of batch composition for BST ($\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$)

Compound Name	Mol. Wt.	Purity (%)	Fraction	Mol. Wt. *fraction	Wt. %	Assay Correction	For 25 g
BaCO_3	197.3359	99.5	0.5	98.6680	39.0999	39.296	9.7449
SrCO_3	147.6289	99.0	0.5	73.8145	29.2510	29.5464	7.3272
TiO_2	79.8658	99.0	1	79.8658	31.6491	31.9687	7.9279
Total				252.3482	100	100.8111	25.0000

3.1.3 Preparation of different glasses

(a) PBBS glass batch preparation: For the preparation of $60\text{PbO}-20\text{B}_2\text{O}_3-5\text{BaO}-15\text{SiO}_2$ (PBBS) glass, different oxides and carbonates (PbO , H_3BO_3 , BaCO_3 and Quartz GR with fractions of 0.6, 0.2x2, 0.05 and 0.15 respectively in weight fraction) were used for preparation of PBBS glass. The raw materials were weighed in stoichiometric proportion (described in Table 3.3) and thoroughly mixed in agate mortar pestle for 4 h. The mixed powder was transferred in an alumina crucible and heated in glass melting furnace up to 1323 K. Molten glass was then quenched at room temperature. After quenching, the glass was crushed into very fine powder particles.

Table 3.3 Calculation of batch composition for PBBS glass

Compound Name	Mol. Wt.	Purity (%)	Mole fraction	Mol. Wt. × fraction	Wt. %	Assay correction	For 25 g
PbO	223.1994	99.9	0.6=0.6	133.9196	75.4340	75.5095	18.8440
H_3BO_3	61.8330	99.5	0.2×2=0.4	24.7332	13.9317	14.0017	3.4942
BaCO_3	197.3359	99.5	0.05=0.05	9.8668	5.5577	5.5868	1.3942
Quartz GR	60.0843	99.95	0.15=0.15	9.0126	5.0766	5.0792	1.2675
Total				177.5323	100.00	100.1771	25

(b) Bismuth borate glass batch preparation: The $\text{Bi}_2\text{O}_3-\text{B}_2\text{O}_3$ (BB) glass was prepared by mixing different oxides ($2\text{H}_3\text{BO}_3$ and Bi_2O_3) in stoichiometric weight percent (Table

3.4). The mixed powder of BB was put in an alumina crucible. The crucible was put into a glass melting furnace, which melted the sample at 1123K. The molten glass was quenched at room temperature. After quenching, solid glass was crushed into fine particles.

Table 3.4 Calculation of batch composition for BB glass

Compound Name	Mol. wt.	Purity (%)	Mole fraction	Mol. Wt. × fraction	Wt. %	Assay correction	For 25 g
Bi ₂ O ₃	465.9590	99.0	0.45×1=0.45	209.6815	75.5071	76.2698	18.9000
2H ₃ BO ₃	61.8330	99.5	0.55×2=1.10	68.0163	24.4929	24.6160	6.1000

3.1.4 Liquid phase sintering of barium strontium titanate

(a) **PBBS glass added BST:** 0 - 10 wt% of PBBS glass was mixed with the calcined powder of BST ceramic properly to form different batch compositions as described in Table 3.5. The XRD patterns of calcined powder confirm the formation of BST phase which has been described in section 4.2.3 of chapter 4. Small amount of 4% Polyvinyl Alcohol (PVA) solution was used as a binder. The mixed powders were then pelletized by hydraulic press in cylindrical and rectangular die-cast under the load of 60 KN. The pellets were heated up to 723K for 1 h in first step to remove binder and then sintered in the temperature range 1148 - 1553K for 2 h with the heating and cooling rate of 5K/min in the PID controlled electric furnace. The optimum sintering temperature for different composition is given in Table 3.5. A flow chart for liquid phase sintering of BST ceramic using PBBS glass is shown in figure 3.1.

Table 3.5 Different BST-PBBS batch compositions

S. No.	Sample Name	Sample Composition	Sintering Temperature
1.	BST	BST with 0 wt% glass	1523 K
2.	BST-3P	BST with 3 wt% glass	1223 K
3.	BST-5P	BST with 5 wt% glass	1198 K
4.	BST-8P	BST with 8 wt% glass	1173 K
5.	BST-10P	BST with 10 wt% glass	1148 K

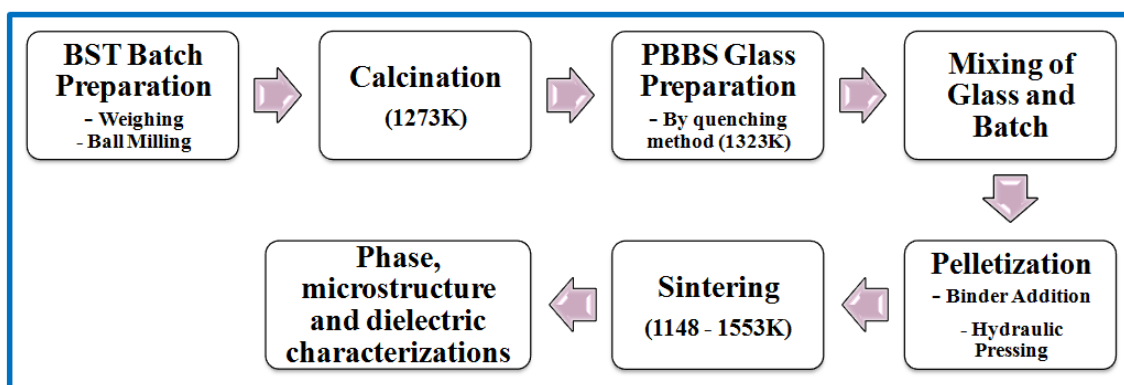


Figure 3.1 Flow chart showing liquid phase sintering of BST ceramic using PBBS glass.

(b) **BB glass added BST:** 0, 3, 5, 8 and 10 wt% of BB glass was mixed with the calcined powder of BST appropriately as described in Table 3.6. Small amount of 3 wt% polyvinyl alcohol (PVA) solution as a binder was added properly in mixed powder and thoroughly mixed with the help of mortar pestle. The mixed powder was then pelletized by hydraulic press cylindrical die-cast under the load of 70 KN. The pellet was sintered at 1173 - 1423K for 3 h at the heating and cooling rate of 4 K/min in an electric furnace. The optimum sintering temperature for different composition is given in Table 3.6. A flow chart for liquid phase sintering of BST ceramic using BB glass is shown in figure 3.2.

Table 3.6 Different BST-BB batch compositions

S. No.	Sample Name	Sample Composition	Sintering Temperature
1.	BST	BST with 0 wt% glass	1223K
2.	BST-3B	BST with 3 wt% glass	1223K
3.	BST-5B	BST with 5 wt% glass	1223K
4.	BST-8B	BST with 8 wt% glass	1223K
5.	BST-10B	BST with 10 wt% glass	1223K

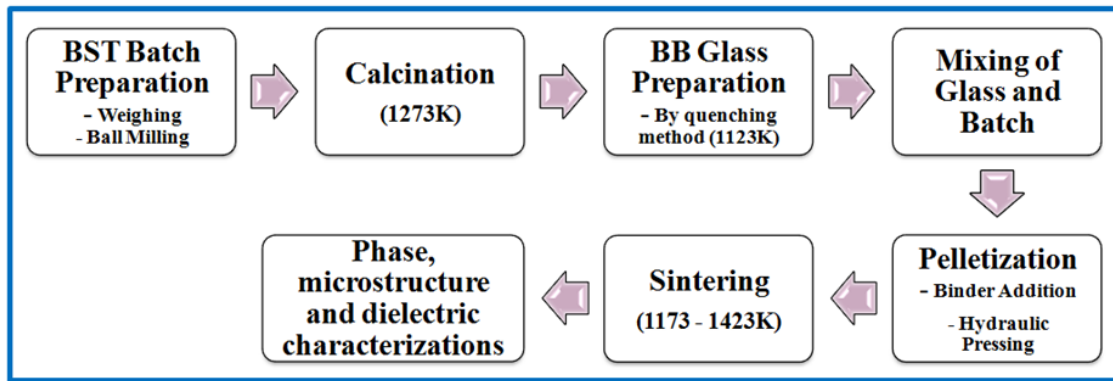


Figure 3.2 Flow chart showing liquid phase sintering of BST ceramic using BB glass.

3.2 Material Characterisation

3.2.1 Thermo-gravimetric (TG) and Differential thermal analysis (DTA)

Thermo gravimetric analysis (TGA) is a technique for measuring the change in weight of a substance as a function of temperature or time. The sample usually a few milligrams in weight is heated at a constant rate and has a constant weight until it begins to decompose at a certain temperature. Under dynamic heating decomposition occurs over a range of temperature and after certain temperature no weight loss is observed leading to the completion of decomposition reaction. The weight losses are fundamental properties of the sample and can be used for quantitative calculations of compositional changes.

In DTA, the material under study and an inert reference are made to undergo identical thermal cycles, while recording any temperature difference between sample and reference (α -Al₂O₃, which does not exhibit endothermic or exothermic effects). Thermocouples are embedded in the test substance and in the α -Al₂O₃ powder and are connected, so that their electromotive force (emf) is opposed, the net emf therefore represents the temperature difference between the sample powder and the inert α -Al₂O₃.

The two capsules are heated at a constant rate and the temperature difference is plotted either against time or against the temperature at some fixed points within the apparatus.

Any physical or chemical change occurring to the test sample, which involves the evolution of heat, leading to an exothermic peak. Conversely, a process, which is accompanied by the absorption of heat, leading to an endothermic peak. The area under any given peak can be used as a quantitative measure of the amount of heat evolved or absorbed by the physical or chemical changes, which occurred.

TG/DTA of batch compositions of BST ceramic as well as PBBS and BB glasses were performed using LABSYSTM Setaram Instrumentation (Serial no: 1-3347-1 DTA/TGA/DSC) from room temperature to 1473K, at a heating rate of 10K/min to determine reaction cum decomposition of BST ceramic and glass transition and crystallization temperature of PBBS and BB glasses.

3.2.2 Phase analysis and rietveld refinement

The phase formation of sintered ceramic samples were investigated by X-ray Diffractometer (Rigaku Miniflex II, Desktop X-Ray D) operated at 30 KV and 15 mA using $\text{CuK}\alpha$ ($\lambda = 1.541836 \text{ \AA}$) radiation with Ni filter within the scanning range $10^\circ - 90^\circ$ (scan rate of $1^\circ/\text{min}$) followed by Rietveld refinement using FullProf_Suite.

Rietveld refinement is a method for structure refinement, which plays great role in the illustration of crystal structure. Fullprof_suite is one of the most popular softwares used for rietveld refinement. Basic idea behind the refinement is to compare actual powder diffraction pattern with software simulation diffraction pattern, then optimize the simulated data of software by varying the parameters, like unit cell coordination, atomic displacement, site occupancies etc. to reach the closest to experimental pattern as much as possible to analyze the actual structural properties of material under test.

Some physical and mathematical parameters indicate the success of rietveld refinement. The most useful physical indicator is the difference plot. It is simply the calculated profile subtracted from experimental data. Some mathematical parameters also indicate the

goodness of refinement, like Rwp (weighted pattern), RE (Expected Factor), RB (R-Bragg factor) etc. The goodness of fit (χ^2) = Rwp/RE is very useful mathematical indicator whose value less than or equal to 2 is considered as satisfactory refinement result.

3.2.3 Microstructure analysis

Scanning Electron Microscopy (SEM) produces micro-structural image of sample through scanning by focused beam of high energetic electrons. The resultant signal coming out from electron-sample interaction reveals the information about sample including crystal structure, orientation of particles within the materials, chemical composition and external morphology (texture). The secondary electrons (SE) excited by electron beam play dynamic role, in order to produce the image of sample. Secondary electrons are created by collision between high energy electron beam and electrons of the sample. Such collision kicks out lower energy electrons from their orbit. These lower energy electrons play dominant role in drawing the image of sample. The surface morphology of all the sintered samples was carried out using Scanning Electron Microscope (ZEISS Instruments). All the pellets were first polished thoroughly with SiC emery papers of different grades along with the diamond paste on velvet cloth. After that, these samples were chemically etched (10 % HF + 10% HNO₃) for 15 seconds. Chemically etched pellets were gold coated using “Hummer” sputtering coating unit.

3.2.4 Density

Density of glass samples and sintered ceramics was determined using Archimedes principle. Distilled water is used as a liquid. The density is calculated using the formula:

$$\text{Density} = \frac{w_d}{w_a - w_s} \quad (3.1)$$

where w_d = weight of dry sample, w_s = weight of sample suspended in water after boiling it for 2 h and w_a = weight of water absorbed in the sample. The weighing balance used for the weight measurement is having the accuracy of $\pm 0.0001\text{g}$.

3.2.5 Dielectric measurements

(a) **Microwave dielectric characterisation:** The dielectric measurements in the microwave frequency range (8.2 - 12.4 GHz) were performed using Nicholson-Ross-Wier (NRW) technique [Smiljanic et al. (1997)] with the help of Keysight Technologies make Network Analyzer (ENA Model E5071C) with X11644A calibration kit. The X- band waveguide dimensions are $22.86\text{ mm} \times 10.16\text{ mm} \times 5\text{ mm}$.

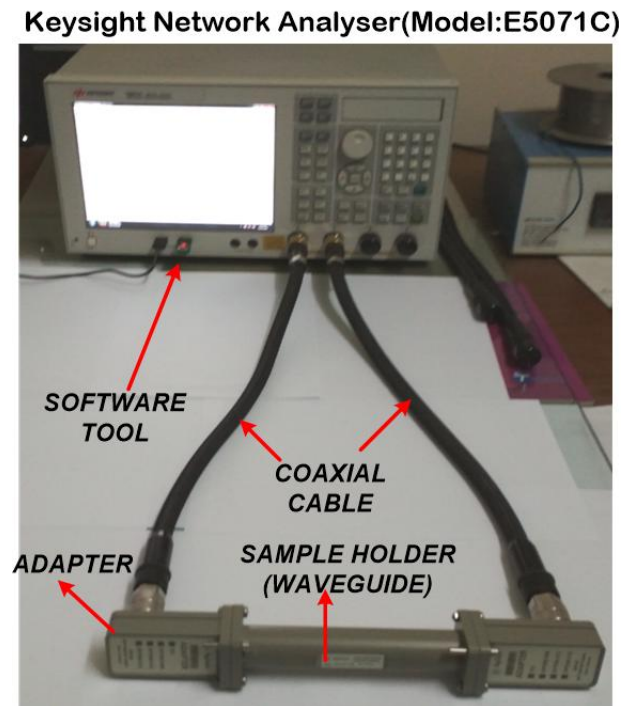


Figure 3.3 Microwave dielectric measurement of the sample using Network Analyser.

(b) **Low frequency dielectric characterisation:** The dielectric properties of the prepared ceramics were determined over a frequency range 1Hz - 1MHz. The specimens were tested by parallel plate capacitor method using Novocontrol Alpha-A High Performance Frequency Analyzer in the temperature range 293 - 450K and by LCR meter (Agilent E4980A Precision) in the cryo-temperature range 20 - 293K.

3.3 Design and Simulation of DRAs

The components for the design of DRAs: substrate (FR4), ground plane, resonator segment (ceramic) and feeding structure. Antenna resonator can have different standard geometries, such as cylindrical, rectangular, triangular, hemispherical and spherical made of different dielectric ceramic materials ($\epsilon_r = 5-50$). In the present investigation, three antenna geometries i.e. rectangular, cylindrical and filleted were used and two different excitation schemes i.e. Micro-strip line fed aperture coupling (described in chapter 5) and composite feed (probe plus Ex-OR patch feed) described in chapter 7, were employed.

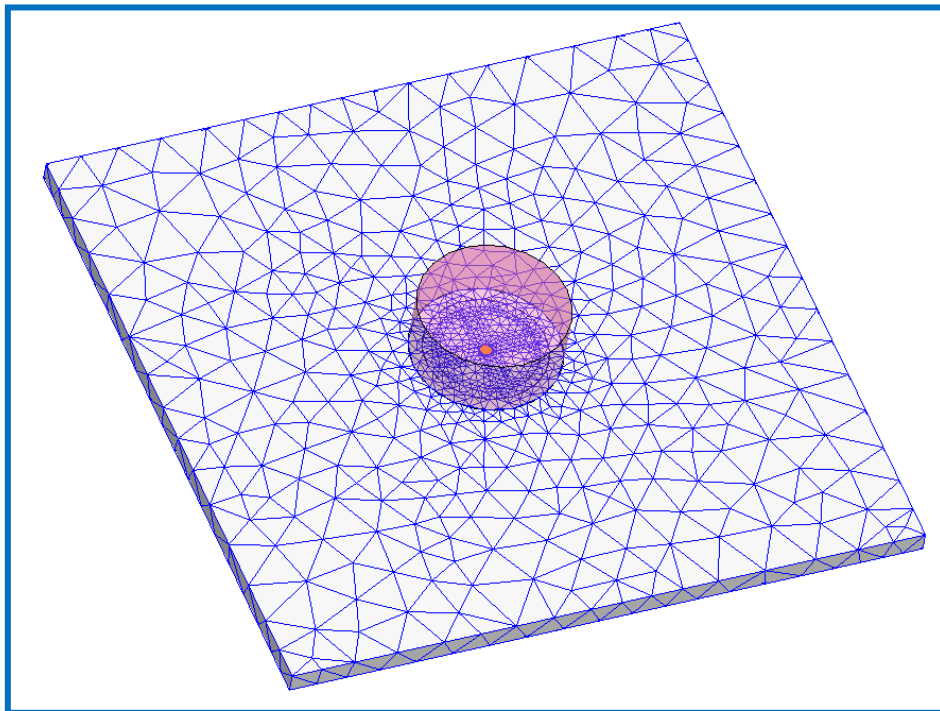


Figure 3.4 Depiction of mesh on the FR4 substrate of the composite feed CDRA using HFSS software.

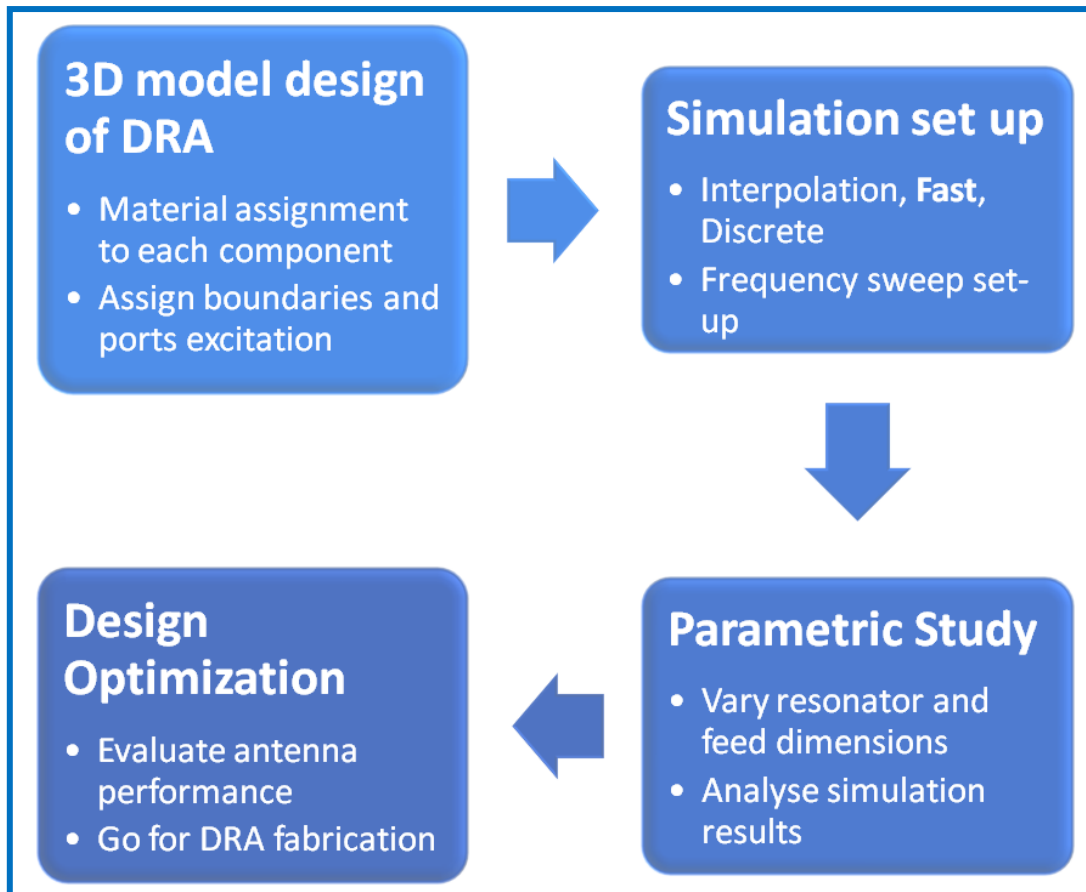


Figure 3.5 Design procedure used for antenna simulation using HFSS software.

For the design of DRAs, Ansys High Frequency Structure simulator (HFSS) software was used. Ansoft HFSS employs finite element method (FEM), adaptive meshing (as shown in figure 3.4) and brilliant graphics to give the unparalleled performance and insight to all 3D electromagnetic problems. Figure 3.5 shows the procedure for DRA design using HFSS software. The detailed design steps followed in HFSS are given below:

- (a) Preferably variables such as a , b , c etc. are used for all of its structural dimensions and values are assigned to these variables by considering antenna design equations.
- (b) Material is assigned to each antenna component.
- (c) Do the excitation of the port
- (d) Draw air box and assign it as radiation boundary.

- (e) Do frequency sweep setup in which wide frequency range is defined in such a way that the desirable antenna operating bandwidth lies within this range.
- (f) Three iterative techniques: Interpolation, fast and discrete. For the parametric study, fast iteration is generally preferred. Specify, different antenna parameters, such as feed dimensions, material dielectric constant, and antenna resonator dimensions, and perform simulation study.
- (g) After optimization, go for discrete iteration for obtaining final simulation results. Discrete iteration gives accurate results but takes more time for its operation. So, it can be verified for short range of operating frequencies only.
- (h) Extract different antenna characteristics such as reflection coefficient (S_{11}) – frequency characteristic, far field radiation pattern in different planes, 3D gain and near field distribution. With the results obtained, analyse the antenna performance. If it is good, go for antenna fabrication for the optimized design.

3.4 DRA Fabrication

3.4.1 Requirement

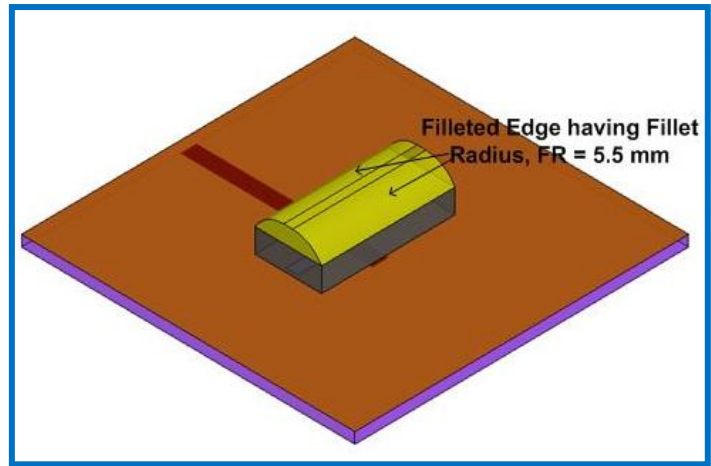
For the design of filleted rectangular DRA (investigated in chapter 5) and composite feed cylindrical DRA (investigated in chapter 7), FR-4 was used as the substrate. The cylindrical ceramic pellet ($\epsilon_r = 17$, diameter = 11.5 mm and height = 5.0 mm), teflon (10 mm × 20 mm × 3.5 mm) and filleted ceramic pellet (dimensions = 10 mm × 20 mm × 2.5 mm) with fillet radius of 5.5 mm are prepared for the design of two antennas. Other requirements include coaxial connector probe (3.2 mm SMA), PCB printing machine (LPKF Laser & Electronics, Model: ProtoMat S103), soldering kit and araldite adhesive.

3.4.2 Fabrication steps

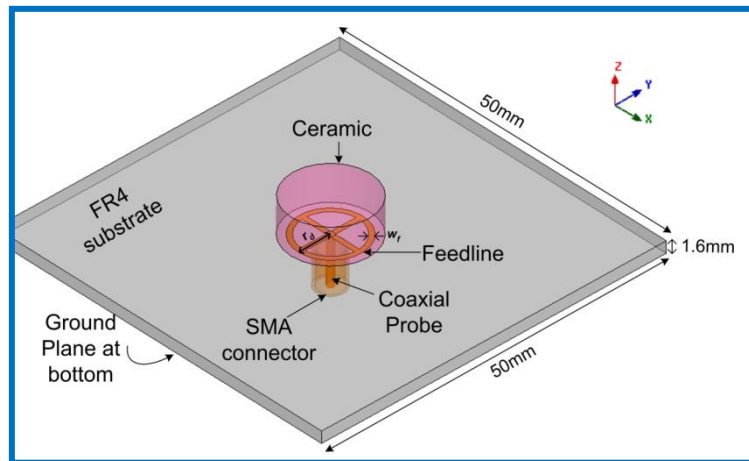
- (a) **Fabrication of filleted RDRA:** The copper clad FR4 sheet of dimensions 50 mm x 50 mm x 1.6 mm was taken as the substrate. On its upper side, the copper is etched out

for creating a slot (dimensions = 18.9 mm x 1.8 mm) leaving behind the ground plane and on the lower side, the copper is etched out for only the feedline of the dimensions 28.9mm x 2.5mm, using the PCB printing machine. The antenna consists of two segments i.e. rectangular teflon and filleted BST-3P ceramic. The 3D geometry of the filleted RDRA is shown in figure 3.6(a). All the optimized antenna dimensions are given in Table 5.1 of chapter 5.

(b) Fabrication of composite feed cylindrical DRA (CDRA): The copper clad FR4 sheet of dimensions 50 mm × 50 mm × 1.6 mm was taken as the substrate. On one of its side, the copper is etched out leaving behind the printed patch of optimum dimensions $w_f = 0.7$ mm and $r_d = 4.7$ mm. The PCB printing machine was used to etch out copper from the undesired portion of the substrate with the accuracy of 0.1 mm. On the bottom side (i.e. ground), a very small circular area of diameter (1.5 mm) was also etched out in the central region from where the excitation probe is to be inserted into the substrate through a small hole. This is done to avoid the contact of the centre conductor of the SMA connector with the ground. The coaxial excitation probe (SMA) was inserted from the bottom side of the substrate, with its outer conductor touching the ground plane and the inner probe length going up to the full height of the substrate exactly at the centre of the feedline patch. Upon the feedline patch, the ceramic segment is fixed as shown in figure 3.6(b).



(a)



(b)

Figure 3.6 3D geometry of (a) Fillet RDRA and (b) composite feed CDRA.

Keysight make Network Analyzer (E5071C)

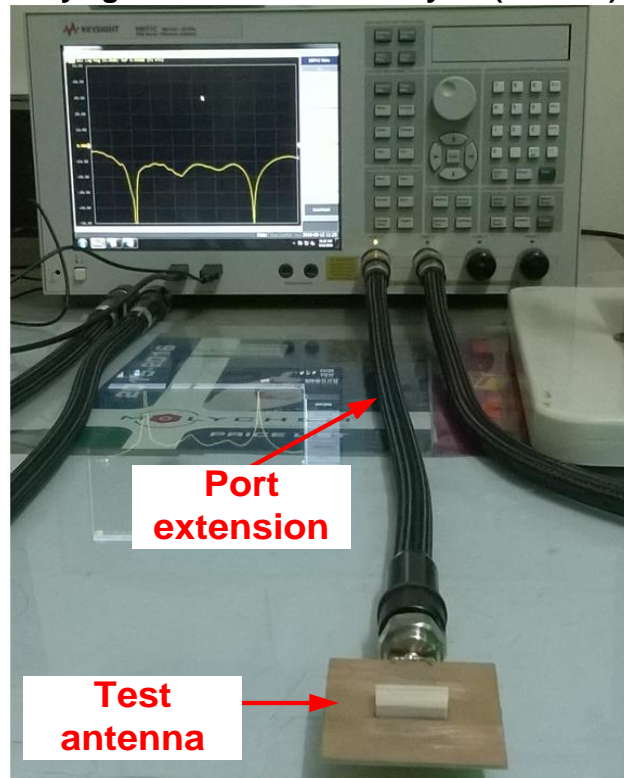


Figure 3.7 Measurement of reflection coefficient (S_{11}) – frequency characteristic of the fabricated prototype of DRA through Network Analyser

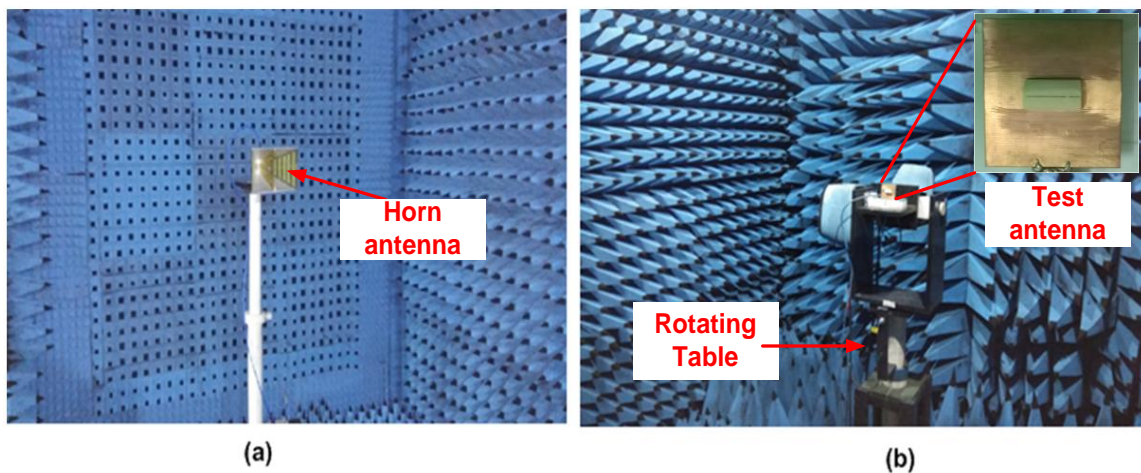


Figure 3.8 Experimental setup for measurement of radiation characteristics of the fabricated prototype of DRA.

3.5 Antenna Measurement

For measurement of reflection coefficient – frequency characteristic of the test antenna, Keysight make Network Analyser (Model: E5071C) (Figure 3.7) was used.

For obtaining radiation characteristics i.e. radiation pattern and gain of test antenna, measurement was made in the anechoic chamber (Figure 3.8). The test equipment connected with the measurement system is the Agilent Technologies make Network Analyser (Model: N5224A). For the radiation pattern measurement in the two planes, the test antenna acting as receiving antenna was rotated in both the azimuthal (horizontal plane) and the elevation (vertical) planes in the far field region while keeping standard wideband transmitting horn on the other side.