

# Preparation and Structural Characterization of CCTO: Silica Ceramic Glass 0:3 Connectivity Composite

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## Abstract

CCTO or  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  is a wonder material exhibiting enormous dielectric constant but with unusually large dielectric losses. Considering the importance of the material in charge storage devices, it is the need of the hour to prepare and characterize stable ceramics as well as its composites. The ceramics were synthesized using the solid state sintering method, while the composites of the ceramic with silica ( $\text{SiO}_2$ ) were prepared by mixing the ceramic in silica and vitrifying the silica matrix. 0:3 composites of CCTO and silica glass was formed by changing the ratios of the two phases. The plant material sources also had CCTO and silica which produce the dielectric current which helps to trap the sun light photons.

**Keywords:** CCTO, Dielectric, Manufacturing, Vitrification, Silica, Ceramics.

## Introduction

$\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  (CCTO) ceramics have been widely studied due to its extremely large dielectric constant and consequent enormous charge storage capacities with respect to its volume<sup>[1]</sup>. Hence the material possesses huge potential in energizing future vehicles and machines which requires intermittent surges of power at various stages of its operations. One may design super capacitors, with this ceramic, which occupies very small space but has the capacity to release large enough charges at will and drive heavy machines or vehicles<sup>[2,3]</sup>. Super capacitors supplement the storage batteries and therefore can be used in tandem with the energy system.

In the present study, CCTO ceramics and the composites were prepared using standard procedures mentioned in the literature with some modifications, discussed elaborately in experimental section. Silica ( $\text{SiO}_2$ ) or silicon dioxide in its glassy form (amorphous) was used as a matrix for preparing the composite. This diphasic composite in its 0:3 connectivity<sup>[4]</sup> was decided upon due to the following reasons. First of all, micro-particles of CCTO ceramic needed an even distribution in thermal, mechanical and chemically stable matrix. Silica is chemically inert with respect to CCTO and corrosive environment. The glassy state of silica can be achieved within a short period of time<sup>[5]</sup>, hence manufacturing of the composite is not overly time consuming. The infrastructure for glass manufacture, including trained manpower is easily available. Silica as a raw material is ubiquitous, hence cheap. The compatibility of silica glass with silicon is an added advantage, due to ease of integration into electronic devices, where silicon is the base material. In the diatomic dust silica is in rich amount. It is useful to help in the sintering. The characterization of the composites was carried out using standard procedures and instruments, mentioned elaborately in the next section.

## Objectives of the Study

1. CCTO ceramics utilization for manufacturing the glass wares.
2. Good quality and light glass instrumentation.
3. Silica compositions uses in the medical field.
4. Making goods in the Vehicle industries.
5. Making good quality optical fibers.
6. Good quality of articles used in labs.

## Material & Methods

### Preparation of CCTO Ceramics

CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> polycrystalline ceramics were prepared by solid-state reaction [6]. The materials used for preparing CCTO ceramic powder were as follows:

1. CuO (Copper Oxide, ≥99.90%)
2. CaO (Calcium Oxide, ≥99.95%)
3. TiO<sub>2</sub> (Titanium Oxide, ≥99.7%)

All the above materials mentioned in the list were procured from Sigma Aldrich. The powders of the above materials were weighed in stoichiometric proportions before being ball milled in a cylindrical mill lined with rubber and containing zirconia balls. The ball milling has been carried out for at least 24 hours with acetone as the dispersant. The ball milled powder was then sieved using a 5 μm mesh. The sieved powder was compacted lightly in a crucible made of high grade alumina. The mixed powders were then poured in a crucible and loaded into an electrical programmable temperature-controlled furnace, strictly following the steps mentioned below:

#### Step I:

Once the crucible was loaded into the furnace, it was programmed in segments of ramp and soak routines. Initially it is set to reach 500°C from room temperature in 3 hours' time interval and followed by a soak time of 2 hours at 500°C. This is to drive away traces of acetone, organics and other contaminants that may be present during the milling.

#### Step II

After the above step is completed the furnace temperature is raised to 850°C from 500°C and set to reach this elevated temperature in a time interval of 2 Hrs and then programmed to hold at 850°C for an hour. This step is called the calcination step. It is during this phase the solid state reaction between the constituent oxides gets initiated and the product CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> starts to form.

#### Step III

Finally, the furnace is set to a higher temperature of 1250°C from 850°C and programmed to reach the set point in 2 hours and stay at the higher level for 12 hours (soak time). This stage is the most crucial because any snag at this point will render the sample unsuitable for composite development. Also it is during this processing stage a complete transformation to CCTO ceramic occurs, in other words sintering takes place. Sintering time and temperature determines the grain size of the formed ceramic. The soak time is kept this long so that no reactants remains unutilized. The furnace is now allowed to cool naturally to room temperature by either shutting it off; or by controlled cooling using the programmable device.

The ramp soak routine of the furnace is shown as a plot of temperature vs. time in figure 1 below-

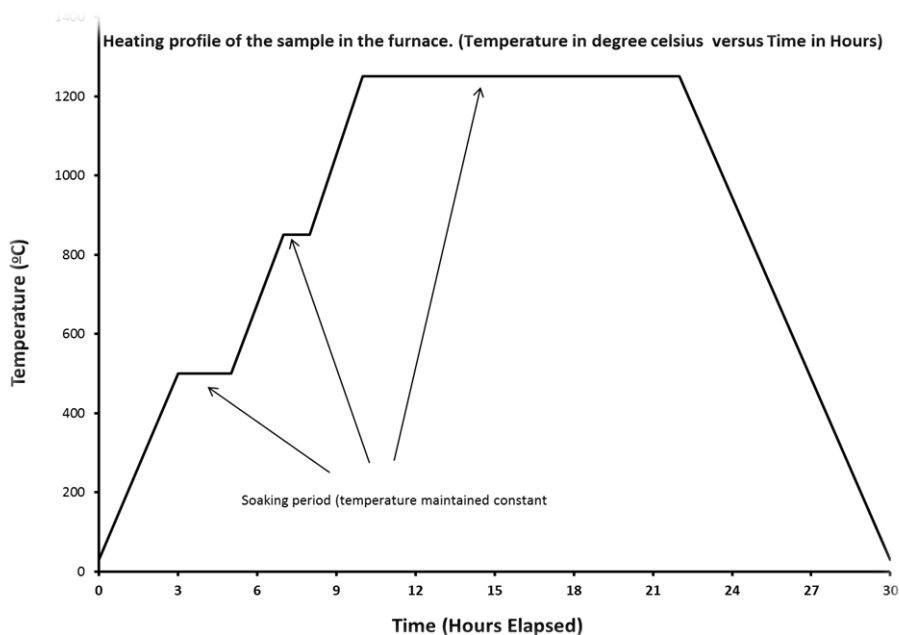


Figure 1 Time –Temperature Plot indicating different steps / segments of PID controller

The furnace used in the study was controlled by a PID controller and the temperature sensor used to measure the instantaneous temperature was a platinum rhodium thermocouple. The furnace was fitted with Molybdenum Disilicide heating elements and was able to reach a maximum temperature of 1800°C.

After the heating process was over the alumina crucible was taken out of the furnace and the ceramic lump formed was removed, crushed in an Agate mortar using an agate pestle. The crushed granules were again ball milled for 12 hrs and the fine powder thus formed was sieved using 5μm mesh. This yields a fine powder of CCTO with the required particle size.

## Preparation of the Composite

The materials used for preparing the composites were as follows:

1. CCTO powders prepared in the lab as mentioned above
2. Silica Powder.
3. Acetone and PVA (poly vinyl acetate)

## CCTO

Silica Glass composites of 0-3 connectivity were prepared by processing sintered powder of CCTO ceramic and Silica. Silica ( $\text{SiO}_2$ ) was procured from Sigma Aldrich; the powders were weighed according to the required volume ratio. From the density of silica mentioned by the supplier (2.65 gm/cc) on the product sheet the weight corresponding to the volume was calculated. The density of CCTO powder (4.93 gm/cc) was elucidated using standard techniques. The first set of samples were prepared in such a way that the material contains ninety percent (80%) by volume of CCTO ceramic and ten percent (20%) by volume of Silica. The calculated amount of the constituents of the composite (CCTO ceramic powder and Silica) were weighed and mixed thoroughly in a mortar and pestle made of Agate, acetone was added to this mixture to facilitate intimate blending. Slurry of the ceramic and silica was formed, now one assumes that CCTO powder has been evenly distributed into a matrix of silica. To the prepared slurry Poly vinyl acetate (PVA) was added, only 0.5% by weight of the paste was the added polymer. The polymer distributes evenly throughout the volume of the mixture, and acts as a binder during further processes. The resulting slurry was poured into a rubber lined zirconia ball mill and was milled for 10 hours at a stretch. The consistency of the slurry was assessed by the amount of time required for the slurry to settle. The more time it takes to settle the better the mixing and hence finer the particles. Had the required consistency not reached it was again ball milled for at least 5 hours. Again the consistency was checked as mentioned. The slurry was then dried by just leaving it in a vacuum oven with moderate vacuum and 70°C temperature. Lumps were formed due to drying of the slurry, these lumps were crushed in an agate mortar into granules and loaded into steel dies (molds) which are designed to withstand high pressures and temperatures, the dies were also air tight so that application of pressure spreads uniformly into the bulk of the material poured into it without any material leaking out of the cavity. The mold loaded with the granules was then heated to 140°C accompanied with a pressure of 25 tones over the cross sectional area of the cavity. The temperature was held for 30 minutes after which the heater was put off and the mold was allowed to cool to room temperature while keeping the applied pressure on. After the mold reaches room temperature, the pressure was released, the mold was then opened and the material inside the cavity was removed. We thus obtained a green sample of the CCTO: Silica glass ceramic composite with a connectivity of 0-3. The cavity of the die was circular with a diameter of 2 inches (50 mm), therefore the shape of the sample was like a disc with appropriate thickness. The

thickness of the composite samples could be varied by adjusting the amount of granules being poured into the die. Since the diameter of the composite sample made with the above mentioned die / mold is a constant and therefore it cannot exceed 50 mm, more amounts of granules will only result in a thicker composite sample. Calculated amount of granules was loaded into the mold so that the resulting sample yields a thickness not more than 1.5 mm. One can in principle mold the material into any desired shape and size using this procedure. All it needs is a mold with the design features as mentioned and a cavity of the desired shape.

## Observations

In the present work the samples were chosen in the shape of thin discs with thickness not more than 1.5 mm. The green samples were then placed in the oven to be vitrified. The temperature of the oven loaded with the green sample was gradually increased to 1000°C so that the green samples do not develop any cracks due to rapid heat shocks. When it reaches 1000°C it is kept soaked in the heat for an hour before it is rapidly cooled to room temperature. Verification results and ceramic glass composite is formed<sup>[7]</sup>. The composite samples were lapped and polished so that discs of about 1.3 mm thickness with flat surfaces perfectly parallel to each other were formed. The samples for SEM were coated with Gold on its plane sides (faces) using a vacuum coating unit (Sputtering unit), because the composite samples were electrically non conducting. Care was taken to mask away the gold electrodes from the edges of the samples. That is the gold electrode coated onto the samples had a diameter 2mm less than the diameter of the sample. The procedure mentioned above<sup>[8]</sup> was repeated for samples of composition 80% , 50%, and 30% by volume of CCTO. Some pure CCTO and silica samples were also prepared possessing the above geometry.

## SEM Studies

The scanning electron micrographs (SEM) of the composites samples as well as pristine CCTO and Silica glass were recorded on an XL30 Philips, USA system. SEM shows the morphology of the samples. SEM is a plot of back scattered electron current intensities, resulting from focusing a high energy scanning electron beam onto the sample surface. The accelerating voltage of the beam and its scan speed decides the resolution of the micrographs. SEM of the composite sample reveals the distribution of CCTO particles within the Silica glass matrix. The connectivity pattern of the composite samples can be literally seen from the SEM micrographs. SEM of the composite sample helps to find whether there is a limiting ratio beyond which the composite loses its 0:3 connectivity configuration. Since the samples were electrically insulating the sample face was coated with metallic gold using a Denton Desk II sputtering system under a vacuum of  $10^{-5}$  mm of Hg at 40 mA and for 30 sec. The magnification chosen for SEM was 20K and the accelerating voltage, EHT-15kV<sup>[9]</sup>.

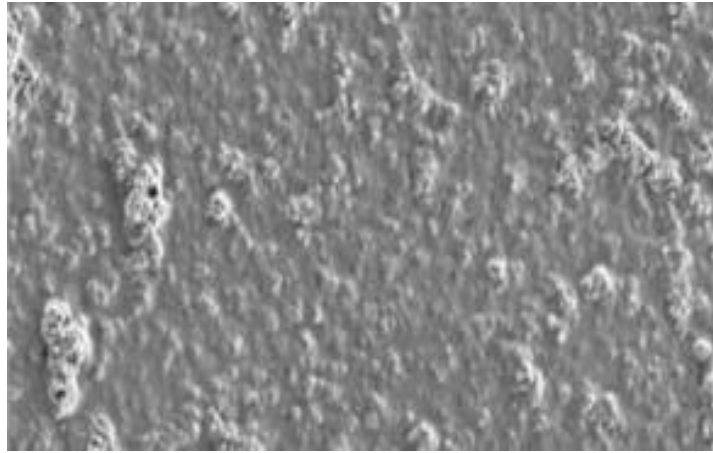
## X-Ray Diffraction Studies

The X-ray powder diffraction pattern of CCTO ceramics and its various composites samples

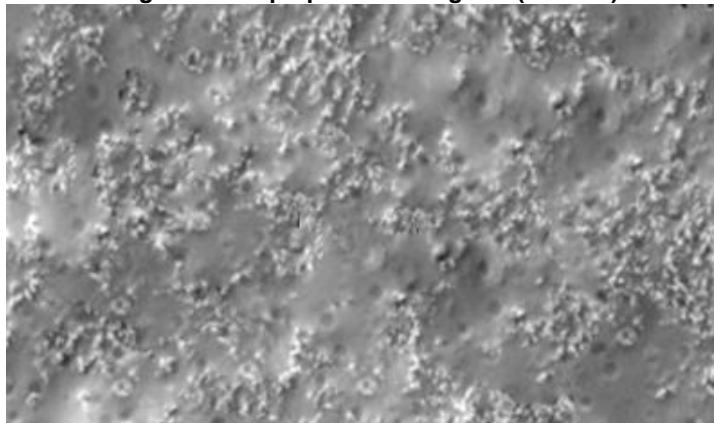
were recorded on a Rigaku X-Ray Diffractogram with Cu  $K_{\alpha}$  line as the probe beam filtered by graphite<sup>[10]</sup>. The wave length of the  $K_{\alpha}$  beam is  $\approx 1.5 \text{ \AA}$ . CCTO ceramic is a well-studied material and therefore the powder diffraction data was easily available. The

JCPDS (PDF#01-075-2188) file was compared with the peaks obtained from the diffractogram. Silica Glass being amorphous does not yield any peaks. Any peaks corresponding to quartz (crystalline form of silica) indicates the start of crystallization.

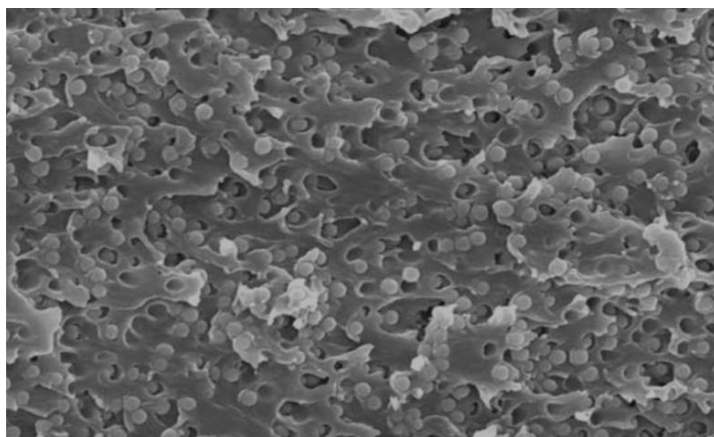
**Fig 2: SEM of prepared CCTO Ceramic (sintered)**



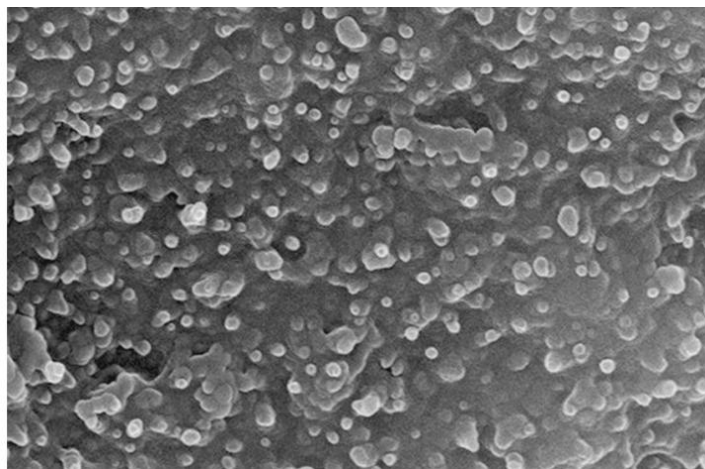
**Fig 3:SEM of prepared Silica glass (vitrified)**



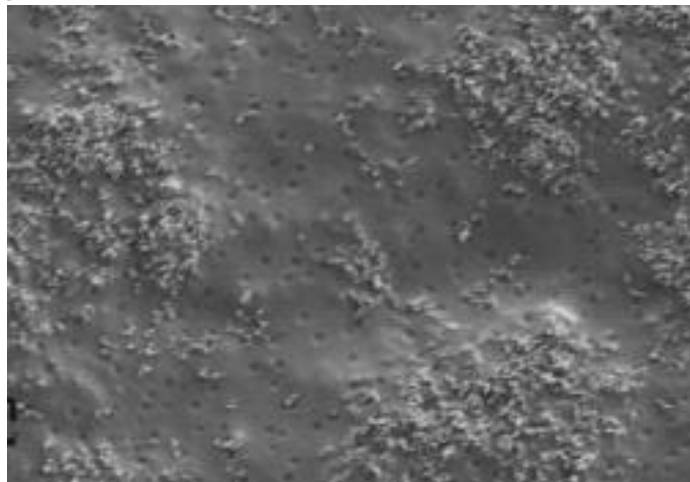
**Fig 4: SEM of 30% CCTO 70% Silica, Ceramic Glass Composite**



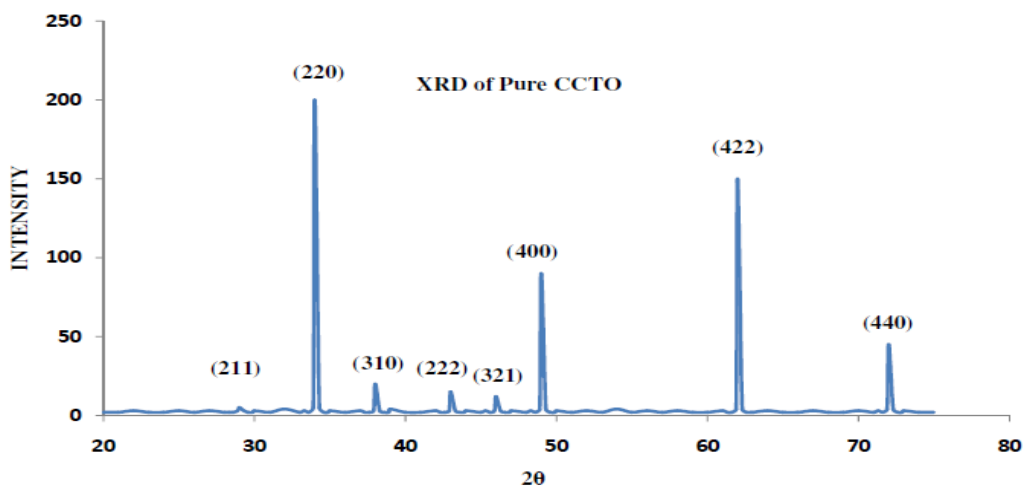
**Fig 5: SEM of 50% CCTO 50% Silica, Ceramic Glass Composite**



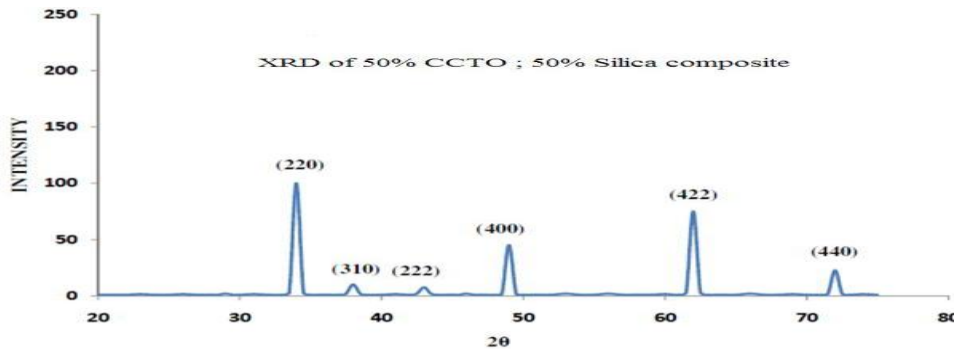
**Fig.6: SEM of 80% CCTO 20% Silica, Ceramic Glass Composite**



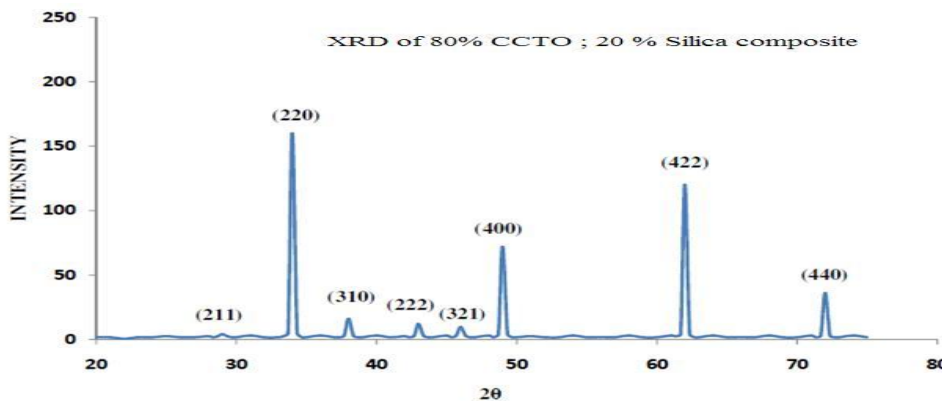
**Fig 7: X-Ray Diffraction pattern of pure CCTO**



**Fig 8: X-Ray Diffraction pattern of 30% CCTO; 70% Silica**



**Fig 9: X-Ray Diffraction pattern of 50% CCTO ; 50% Silica**



**Fig 10: X-Ray Diffraction pattern of 80% CCTO; 20% Silica**

**Result**

The figures 2 to 6 are the SEM micrographs of pristine CCTO ceramic, Silica glass, 30% CCTO composite, 50% CCTO, and 80% CCTO respectively. Here for example 30% CCTO composite implies that the composite contains 30% by volume of the ceramic CCTO and the rest 70% by volume forms the matrix Silica glass. It can be readily observed from the micrographs that the composites (represented by Figs. 4,5 & 6) exhibits an irregular morphology, vis-à-vis pristine CCTO or silica glass. Fig. 4. clearly indicates the formation of a 0:3 ceramic glass composite with CCTO particles which appears like spherical globules distributed throughout the glass matrix. It also exhibits porosity<sup>[11]</sup>, which is practically absent in Fig. 5 and 6. This implies that a lower level of CCTO in a composite allows pore formation which is not a desirable feature in device manufacture. On the other extreme, higher levels of CCTO also yields poor composites, because the CCTO particles (active phase) do not get separated from one another leading to breaking of desired symmetry, which is evident from Fig. 6. Focusing our attention on Fig. 5. i.e. 50% CCTO, one can arrive at a conclusion that composites possessing almost equal volume ratios of ceramic and the matrix contains no pores / voids and are distributed evenly and distinctly, hence device worthy. A constant magnification and accelerating voltage was set in the microscope, so that one may readily gauge the proximity of CCTO particles within the composite as a function of ceramic volume percentage.

Figures 7 to 10 are the X-ray powder diffractograms of pristine CCTO ceramic and its composites respectively. Silica glass does not give any diffraction pattern because of its amorphous nature. The diffractogram of silica glass is an even background haze, no appreciable intensity profile is displayed. Unlike SEM micrograph which is a plot of the sample surface asperities, X-ray diffractograms (XRD) are investigations of the bulk material. The XRD gives atomic level arrangements by delving deep into the material and therefore are more reliable to study the microstructure of a given solid.

Fig.7. represents the XRD of pure / pristine CCTO ceramic (sintered). The hkl planes were indexed using JCPDS file of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  as mentioned in the previous, experimental, section. The file was readily available and therefore the indexing was carried out by comparing the intensity peaks at various values of  $2\theta$ . Some of the distinct and pronounced peak of CCTO is the hkl  $\approx$  (220) at a  $2\theta$  value of  $\approx 34^\circ$ , (400) at  $48.5^\circ$  etc. The other distinct planes are (310), (222) and (321) which are but not very intense, yet specific to CCTO. The carefully indexed XRD of all samples were compared with each other as well. From the figures 8,9 and 10, which are XRDs of composites, it can be observed that as the amount of glass in the matrix increases the intensities from the hkl planes drops. The reasons attributed to the reduction in intensities are firstly the haze from the amorphous silica suppresses the less intense peaks, secondly there is less amount of CCTO particles



coming in the way of the probe X-ray beam. One can also observe a broadening of the peaks which is linked to the stress induced on CCTO particles by the silica matrix.

#### Discussion

The present study was entirely based on silica glass quality improvement and making conductivity. In the same manner many other workers did the work with other aspects of CCTO as Guerette et al (2015) did the work on Structure and properties of silica glass densified in cold compression and hot compression. Kirti, et al (2020) Conductivity and Dielectric properties of CCTO: Silica 0:3 connectivity ceramic glass composites. Mohsen et al (2016) Reviewed the work on Copper Calcium Titanate (CCTO) Electroceramic: Synthesis, Dielectric Properties, Film Deposition, and Sensing Application. Wang, et al (2008) Processing and properties of CCTO ceramics. Liu, et al (2015) Influence of sintering conditions on microstructure and electrical properties of CCTO ceramics. Arbatti, et al (2007) did the work on Ceramic–Polymer Composites with High Dielectric Constant, Advanced Materials. Wenhui Yang et al.(2011) worked on Nano- and microsize effect of CCTO fillers on the dielectric behavior of CCTO/PVDF composites.

#### Conclusion

The results of the investigation mentioned above leads one to conclude that 0:3 connectivity CCTO:Silica ceramic glass composites are best formed when the volume ratio is chosen close to 50:50. Lesser amount of CCTO ceramic makes the composite porous, while, higher volume fraction of the ceramic in the composite leads to breakdown of 0:3 connectivity.

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