



Structural Properties of CCTO : PVC Ceramic Polymer Composites

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ABSTRACT

The present paper deals with the structural property study of ceramic polymers composite synthesised and their significance. The structural analysis is done by X-Ray diffractogram and Scanning electron micrograph study of ceramic polymer composite synthesized. XRD peaks detect whether polymer is crystalline or amorphous whereas SEM study reveals the surface morphology of the ceramic polymer composites.

KEYWORDS : SEM, X-RD, CCTO, PVC

Introduction:

Ceramic materials are inorganic, non-metallic solids, which consists of an aggregate of randomly oriented crystallites bonded together by ionic bonds and have covalent character.¹ Composite materials are materials that combine two or more materials (a selected filler or reinforcing elements and compatible matrix binder) that have quite different properties that when combined offer properties which are more desirable than the properties of the individual materials.² CCTO:PVC which is ceramic composite have ease of fabrication, low cost and offer good properties such as low thermal expansion and high corrosion resistance.

The dielectric properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ material was first reported by Subramanian et.al in 2000.³ They first reported that large dielectric constants were found in $\text{ACu}_3\text{Ti}_4\text{O}_{12}$ (A= trivalent rare earth or Bi) type material and interpreted the high permittivity in terms of its intrinsic crystal structure, i.e., arising from the local dipole moments which are associated with off center displacement of Ti ions. Ramirez et al. have proposed the collective ordering of local dipole moments as a cause of the unusually high dielectric response and explained the phenomenon by the highly polarizable relaxation excitations.⁴ The XRD and SEM study tells about grain size effect on material when PVC (Poly Vinyl Chloride) is added in CCTO in increasing percentage from 20% to 70%.

Diffractograms peaks indicate the crystallite sizes of CCTO as well as polymer content and indicate that higher percentage of polymer in the composite has a tendency to suppress the CCTO peaks.⁵ The Scanning Electron Micrograph of the composite samples exactly determine the connectivity of the sample

Experimental: $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) polycrystalline ceramics were prepared by solid-state reaction method. The materials used for preparing CCTO ceramic powder were as follows:

1) CuO (Copper Oxide, $\geq 99.90\%$)

2) CaO (Calcium Oxide, $\geq 99.95\%$)

3) TiO_2 (Titanium Oxide, $\geq 99.7\%$)

All the above materials mentioned in the list were procured from Sigma Aldrich. These materials were ball milled in a 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 is then sieved using a 5 μm mesh. The sieved powder has been compacted lightly in a crucible made of high grade alumina. Since the particle size of the constituent oxides plays a major part in the physical properties of the ceramic, therefore sieved powder was again sieved before compaction and sintering. The mixed powders were then poured in a crucible and calcined in an electrical temperature-controlled furnace, strictly following the steps mentioned below:

Step 1: Starting from room temperature, the temper-

ature of the furnace is raised to 500 °C in 3 hours at an even rate; it is then kept constant at 500 °C for 2 hours;

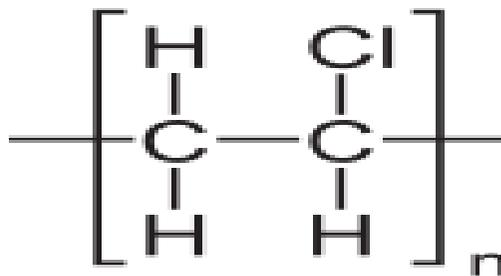
Step 2: The furnace temperature is then raised to 850 °C in 2 hours at an even rate. It is then maintained at a constant temperature of 850 °C for an hour;

Step 3: at last the furnace temperature is raised to 1100 °C from 850 °C in 2 hours at an even pace. It is then kept constant at 1100°C for 2 hours.

The reason for keeping temperatures constant for a few hours at 500 °C, 850 °C is so that any water and alcohol that may still exist in the material will vaporize at these 2 temperatures, while 1100°C is the definite temperature at which the solid state reaction starts. The calcined powders were firstly milled and then sieved. They were pressed into pellets in a cylinder shape of appropriate thickness. The pellets were then put in a high-temperature furnace to be sintered, with the increases in temperature following above steps and then kept constant at 1250 °C for 12 hours. The sintered pellet samples were first polished into a smooth cylinder. Thickness and diameter were then measured using a vernier caliper with an accuracy of 0.05mm. The materials used for preparing the composites were as follows:

CCTO powders prepared in the lab as mentioned.

Poly Vinyl Chloride (PVC).



CCTO: PVC composites of 0-3 connectivity was prepared by mixing pre sintered powder of CCTO ceramic which was prepared according to the method mentioned in section above and PVC procured from Sigma Aldrich. 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 (90%) by volume of CCTO ceramic and ten percent (10%) by volume of PVC. The calculated amount of the constituents of the composite (CCTO ceramic powder and PVC) were weighed and mixed thoroughly in a mortar and pestle made of Agate, this was to minimize the amount of unwanted impurities getting into the bulk of the material prepared. Tetrahydrofuran (THF) is used as a solvent so that a paste of the ceramic and PVC is formed. The paste is now injected into steel dies (moulds) which are designed to withstand high pressures and temperatures, and they are also

air tight so that application of pressure spreads uniformly into the bulk of the material injected into it without any material leaking out of the cavity.

The mould loaded with the paste is then heated to 80^o-140^oC with the pressure on and the pressure gauge reading 25 tonnes. The temperature was held for 30 minutes after which the heater was put off and the mould was allowed to cool to room temperature with the applied pressure on. After the mould reaches room temperature, and the pressure released, the mould is opened and the material inside the cavity is removed. This is now a 0:3 ceramic polymer composite samples. Standard method was followed for elucidation of the microstructure.⁶ The cavity of the die was circular with a diameter of 2 inches (50 mm), therefore the shape of the sample is a circular disc, with an appropriate thickness. The thickness of the composite samples can be varied by adjusting the amount of paste being poured into the die. Since the diameter of the composite sample made with the above mentioned die / mould is a constant and therefore it cannot exceed 50 mm, more amount of paste will only result in a thicker composite sample. Calculated amount of paste was loaded into the mould so that the resulting sample yields a thickness not more than 1.5 mm. One can in principle mould the material into any desired shape and size using this procedure. All it needs is a mould with the design features as mentioned and a cavity of the desired shape. The particle size of the CCTO powder dispersed in the composite was determined using the full width at half maximum of the diffraction peaks in the X Ray diffractograms and substituting in the Debye Scherer formula. SEM measurements are based on the principle of irradiating the specimen with a finely focused electron beam. The secondary electrons, backscattered electrons, auger electrons, characteristic X-rays and several other radiations are released from the specimen. Generally, the secondary electrons are collected to form the image in the SEM mode. The reflected (or back-scattered) beam of electrons are collected, and then displayed at the same scanning rate on a cathode ray tube (similar to a TV screen). The image on the screen, which may be photographed, represents the surface features of the specimen. The surface under study may or may not be polished and etched, but it must be electrically conductive; a very thin metallic surface coating must be applied to nonconductive materials. Magnifications ranging from 10 to in excess of 50,000 diameters are possible, as are also very great depths-of-field. Accessories and equipments permits qualitative and semi quantitative analysis of the elemental composition of much localized surface areas. In the present study the microscope viz. XL30, Philips Co., USA, was used for characterization. The instrument was used under high vacuum conditions. Surface viewing consisted of securing the samples (surface side parallel to the viewing stub) directly to the carbon coated tape. After the sample stubs were mounted, samples were coated with gold (Denton Desk II sputtering system, 40 mA, 30 s). Samples were loaded onto an SEM mount and screwed in the sample holder within the SEM. Vacuum was applied to the instrument and imaging commenced at 10-15 kV and as soon as 1.4 x 10⁻⁵ mm Hg pressure was attained in the SEM. Standard method was followed for elucidation of the microstructure⁶.

Result and discussion:

X-Ray Diffraction Studies:

The x-ray diffractograms are recorded and reproduced below. The x-ray diffractograms of pure CCTO, and composites of 100%, 80% CCTO, 60% CCTO, 40% CCTO and 30% CCTO PVC polymer was recorded as mentioned. The diffractograms are documented in the figures [1 to 5]. The diffractograms were indexed as well as its % CCTO was confirmed. Beyond 40% PVC, it is seen that the peak (321) is completely suppressed by the polymer component in the composite and at 70% polymer even (222) peaks vanish. The broadness of the peak also indicates some strain in the matrix, because grain size of CCTO is the same in all the composite series. Therefore we consider an effective grain size by calculating the apparent size using Debye-Scherer formula or alternatively we can assume an effective shrinkage of grains on addition of more and more polymer to the composite.

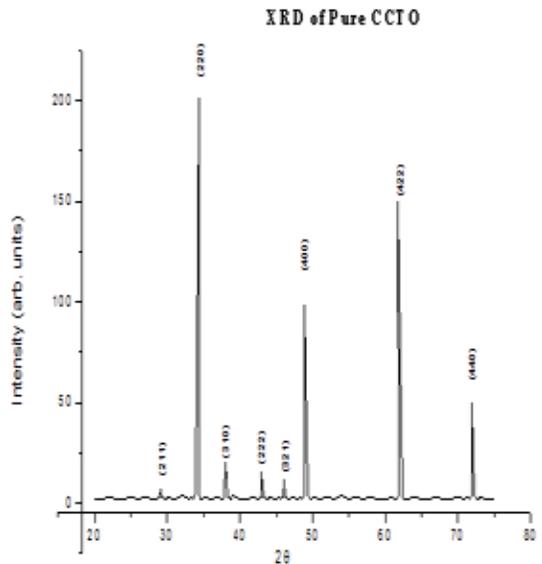


Figure 1: X-ray diffractogram of CCTO ceramic ⁷

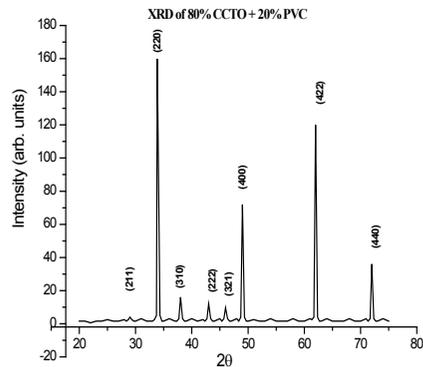


Figure 2 : X-ray diffractogram of 80% CCTO : 20% PVC ceramic polymer composite

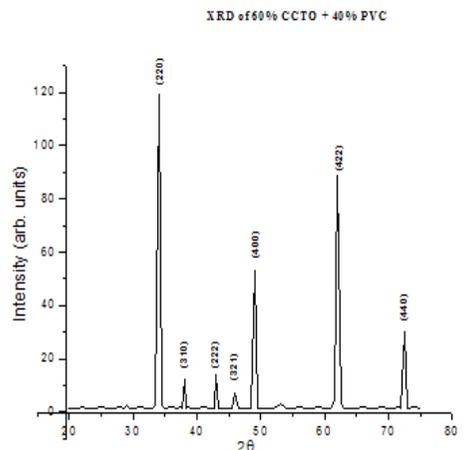


Figure 3 : X-ray diffractogram of 60% CCTO : 40% PVC ceramic polymer composite.

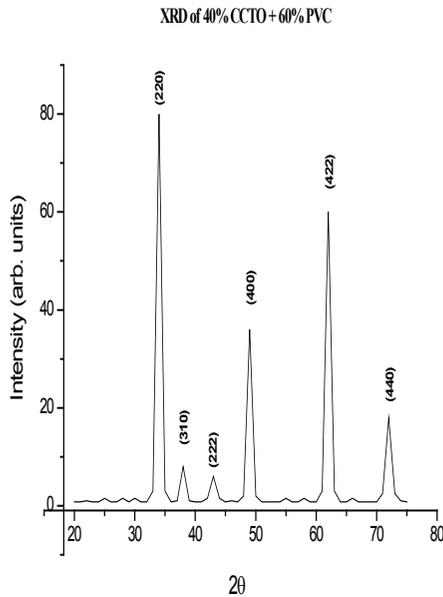


Figure 4 : X-ray diffractogram of 40% CCTO : 60% PVC ceramic polymer composite

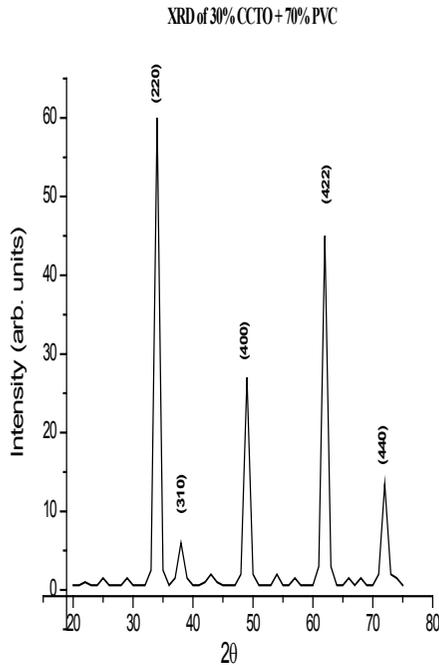


Figure 5 : X-ray diffractogram of 30% CCTO : 70% PVC ceramic polymer composite

SEM Studies:

The Scanning Electron Micrograph of the composite samples was recorded to exactly determine the connectivity of the sample. As different connectivity leads to different end results for the same phase ratios. We have previously assumed the material to possess 0-3 connectivity, the SEMs shall give a direct confirmation of the assumption. The SEMs of PVC and CCTO ceramic in its pristine forms were first recorded, and then the subsequent composites were viewed in the light of the pristine phases. We had tried to maintain the magnification and the wavelength of the electron beam to be uniform. Yet in some cases to enhance the feel of the microstructure we had to change the magnification and wavelength.

Figures 6 to 10 are the SEM photographs of the composite samples.

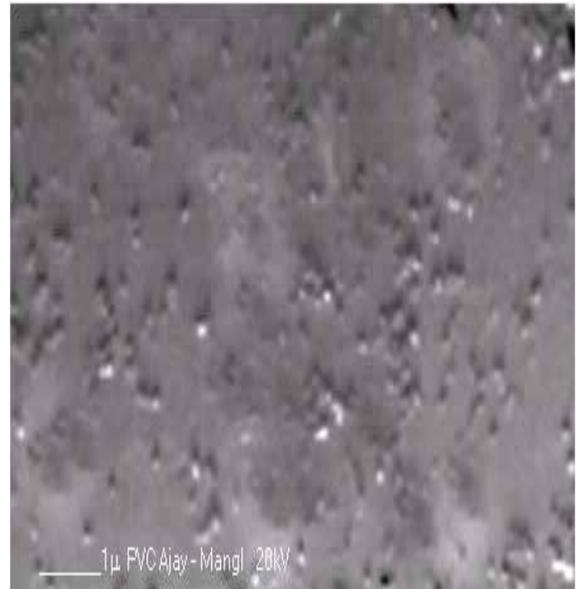


Figure 6: SEM Photograph of pure PVC



Figure 7: SEM Photograph of 70% PVC 30% CCTO Composite

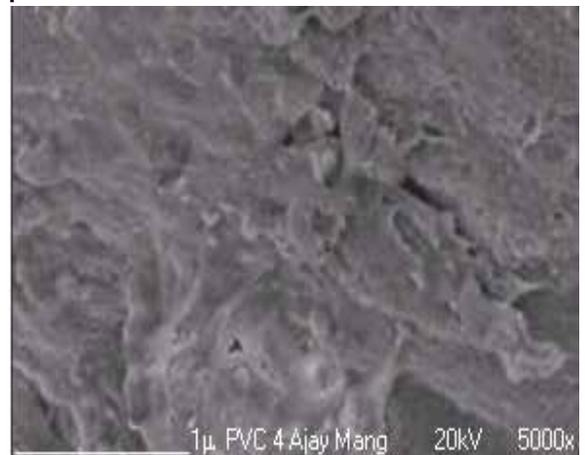


Figure 8: SEM Photograph of 60% PVC 40% CCTO Composite

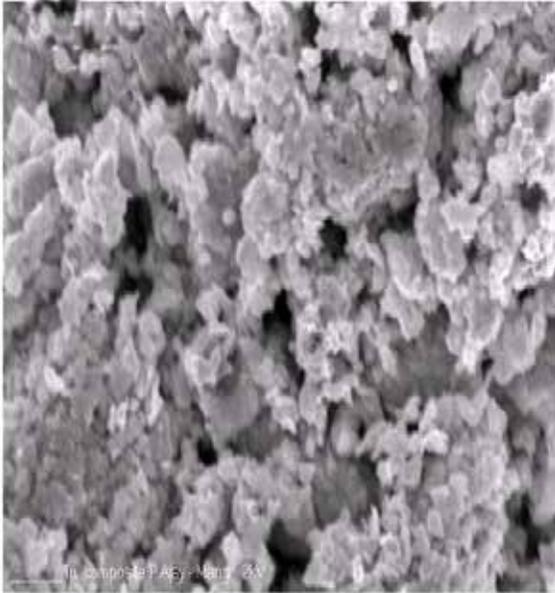


Figure 9: SEM Photograph of 40% PVC 60% CCTO Composite

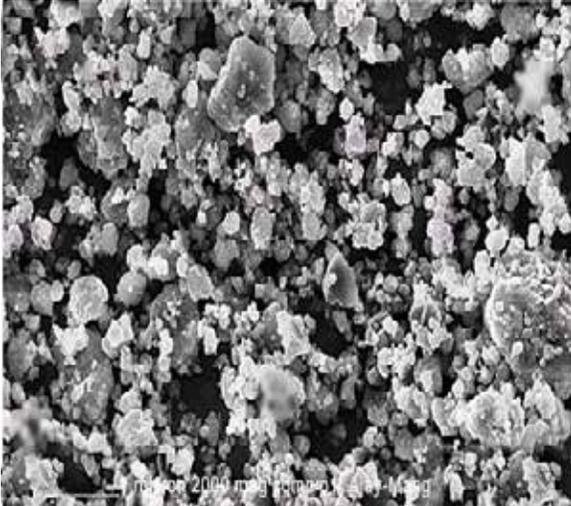


Figure 10: SEM Photograph of 20% PVC 80% CCTO Composite

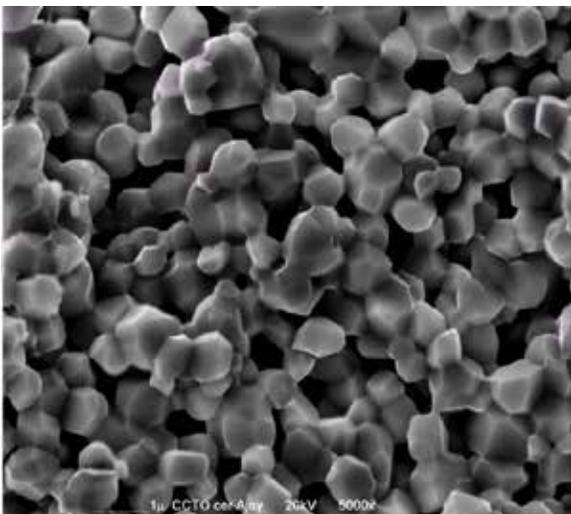


Figure 10 :SEM Photograph of CCTO ceramic

Conclusion:

It is seen from the X-ray diffractograms that the crystalline character of the ceramic phase within the composite gets reduced with more and more percentage of Polymer. It is evident from the X-ray diffractogram of the successive samples that at higher polymer percentages the ceramic particles get strained which in turn affects the grains leading to a broadening of the x-ray peaks. The diffractograms were indexed as well as its % of CCTO was confirmed. The peaks indicate the crystallite sizes of CCTO as well as polymer content. The broadness of the peak in X Ray diffractograms indicate some strain in the matrix, because grain size of CCTO is the same in all the composite series. We have considered an effective grain size by calculating the apparent size using Debye-Scherrer formula⁸. The Scanning Electron Micrograph of the composite samples was recorded to exactly determine the connectivity of the sample⁹. We have assumed the material to possess 0-3 connectivity and the SEMs shall give a direct insight into the material. The SEMs of PVC and CCTO ceramic in its pristine forms were first recorded, and then the subsequent composites were viewed in the light of the pristine phases. It has been found that in order to maintain the magnification, the wavelength of the electron beam needs to be uniform. The representative SEM photographs show expected behaviour of the composites, with respect to its connectivity and morphology. It is indeed a 0-3 connectivity and the morphology is quite even. It has been observed from the micrographs that high percentages of CCTO ceramic leads to clustering of the particles leading to an effectively larger particle size and the samples show associated effects. The effects are corroborated using X-ray studies as well as dielectric spectroscopy.

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