Copper Ion Doped Mullite Composite in Poly (vinylidene Fluoride) Matrix: Effect on Microstructure, Phase Behavior and Electrical Properties

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Abstract: Highly crystallized copper ion doped mullite composites have been synthesized at 1100°C and 1400°C *via* sol-gel technique with five different strengths of copper ion and was incorporated in poly-vinylidene fluoride (PVDF) to make doped mullite composite/polymer films. We have studied the effects of this dopant on microstructure, phase transformation, and electrical properties of the polymer films over a wide range of frequency from 1.0 KHz to 2.0 MHz. Characterizations were done by various analytical tools at room temperature. Prominent mullite phases were observed from XRD, FTIR spectroscopy and FESEM characterization of composite polymer. The concentration of the dopant and the sintering temperature were found to be the two basic factors which affect the phase transition of the polymer. The composite film showed maximum dielectric constant of 19.96 at 1 KHz for 1.2M concentration of copper ion doped mullite sintered at 1400°*C,* compared to 3.09 for the pure polymer. Furthermore, both dielectric constant and electrical conductivity of the composite were found to be highly frequency and temperature dependent. After doping, the A.C. conductivity of the composite was found to increase with increasing temperature following Jonscher's power law and the electrical resistivity reduced too. Moreover, the results revealed that the phase behaviors and micro structural changes of the copper ion doped mullite composite/polymer film affected its electrical properties with possible impact on its applications.

Keywords: Polymer, Mullite, Sol–gel technique, XRD, FTIR, Dielectric properties, FESEM.

INTRODUCTION

Polymorphism is an essential characteristic of Poly vinylidene fluoride (PVDF). PVDF is a semi-crystalline polymer having four crystal polymorphs referred to as α, β, γ and δ phases [1, 2]. Conventional melt and solution processing usually result in α phase which has trans-gauche-trans-gauche (TGTG) chain conformation [3, 4]. β phase has all trans (TTTT) zigzag chain conformation; formation of this phase in PVDF is dependent on stretching of the film as well as the preparation temperature [5, 6]. γ phase has TTTGTTTG' chain conformation which can be achieved by either casting from dimethyl sulfoxide (DMSO) or dimethylformamide (DMF) solution regardless of preparation temperature [7]. High electric field, high pressure and annealing temperatures are also responsible for producing γ phase [8-11].

The main advantage of polymer matrix over ceramic materials is its mechanical quality and it can also be synthesized easily. It has been observed that pure polymer matrix possesses large breakdown strength, good flexibility and great mechanical strength; it is easy

to process but has a very low dielectric constant [12-14]. On the other hand, ceramic composites generally suffer from brittleness which can be reduced to a commendable extent by integrating ceramic composites into the polymer matrix. Micro scale ceramics of high dielectric constant are used as fillers in polymer to increase its dielectric constant [15-17]. For such composites, filler loadings should be high enough for attainment of that range of dielectric constant that is high enough for industrial applications purposes. Though the electrical resistivity of polymer is quite high which makes it suitable to be categorized as an insulator still its electrical properties could be enhanced by incorporation of fillers in polymeric matrix as these fillers interact with the polymer chains. Thus these composites have the ability to exhibit new properties that single phase materials do not possess [18].

Thus, novel composites with comparatively high capacitance, high-energy storage density, and small volume can be prepared, which are known to be very useful materials for varieties of applications in electronics such as, transducers, hydrophones, piezo-sensors, high-charge storage capacitors [19], etc.

Roy *et al*. synthesized highly crystallized mullite composite at 1000°C and 1300°C *via* sol gel technique

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in the presence of transition metal ions such as cobalt, nickel and copper. The results showed with increase in concentration of metals, crystallization of mullite was enhanced. The dielectric constant of the composites followed typical trend observed in ceramic materials i.e., decreased with frequency for all the samples attaining constancy at high frequency (1.5 MHz). Similar nature was observed in case of dielectric loss. Doped mullite nanocomposites showed good dielectric properties at high frequency [20].

According to previous reports, doping of copper ion into mullite affects its microstructure, phase transition, and densification behavior. Roy *et al*. prepared mullite samples doped with 0.002M, 0.02M, 0.1M, 0.15M, and 0.2M of iron, nickel, and copper ion by sol-gel process, which showed that the density of the doped samples increases with the increase of metal ion concentration as well as with the sintering temperature. Copper doped mullite exhibits the highest density of 2.46 g cm^{-3} at 1400°C [21].

Priya and Jog [22] were the first to prepare PVDF–clay nanocomposites. They observed that the addition of organically modified clay resulted in the formation of the β-phase instead of the α -phase upon melt processing.

Here, objective of our research work is to investigate the effect of copper doped mullite on phase behavior and microstructure of polymer, and also to study its electrical properties.

EXPERIMENTAL PROCEDURE

Materials

Chemicals used in the preparation of copper doped mullite precursor gels are: Aluminium nitrate nonahydrate [$Al(NO_3)_3.9H_2O$] extra pure (MERCK, India), Aluminium isopropoxide [$Al(-O-i-Pr)_3$] puriss (Spectrochem Pvt. Ltd., India.), Tetra ethyl orthosilicate [$Si(OC_2H_5)_4$] (MERCK, Germany), Copper (II) nitrate trihydrate [$Cu(NO_3)_2.3H_2O$] (MERCK, Germany), PVDF (Sigma-Aldrich) and N,N-Dimethylformamide (DMF) (Sigma-Aldrich).

Methods

Aluminum isopropoxide (Al(-O-i-Pr)₃) and aluminum nitrate nonahydrate (ANN) were used as alumina sources and tetra ethyl orthosilicate (TEOS) as a silica source. Mullite precursor gel solution was prepared by dissolving stoichiometric amounts of aluminium

isopropoxide and TEOS in the aqueous solution of aluminium nitrate nonahydrate and stirring it vigorously for 2 hours. The molar ratio of Al(-O-i-Pr)₃/Al(NO₃)₃.9H₂O was kept at 7:2 in order to form spinnable sols and the mole ratio of Al/Si was 3:1. Moreover, pH of the solution was also maintained at 5, doped solutions were prepared by adding an aqueous solution of five concentrations of the copper salts- 0.4 M, 0.6 M, 0.8 M, 1.0 M, and 1.2 M to the original solution and stirring it for 90 minutes. The solution takes the gel form after vigorous stirring and overnight heating at 60°C. The samples were then pelletized and sintered at 1100°C and 1400°C for 3 hours in a muffle furnace under air atmosphere (heating rate 10°C/min.).

To make PVDF solution, PVDF (10wt%) was dissolved completely in dimethylformamide (DMF), and was stirred at 70°C for 6-7 hours. Copper ion doped mullite samples of different strengths were added to the solution and stirred overnight at above mentioned temperature. The films were prepared with mass fractions of copper doped mullite of 20%. Then it was sonicated in a bath type sonicator for an additional hour to further enhance the dispersion and to eliminate air bubbles simultaneously. Then the ultimate solution was cast and incubated in an oven at 70°C for 1-2 hours until film forms. The complete process has been shown in the form of a flowchart in Figure **1**.

Investigating Instruments

The crystalline phases developed in the samples sintered at room temperature were analyzed by X-ray powder diffractometer (model-D8, Bruker AXS, Wisconsin, USA.) using Cu Kα radiation- 1.5418 A° and operating at 40 KV with a scan speed of 1 sec. /step.

The characteristic stretching and bending modes of vibration of chemical bonds of samples were effectively evaluated by FTIR spectroscopy (FTIR-8400S, Shimadzu) by using air as background from 1200 to 400 cm^{-1}.

Electrical properties such as dielectric permittivity (ε_r), dissipation factor (tan δ), a.c. conductivity ($\sigma_{a.c.}$) and resistivity (ρ) of the samples were measured in the frequency range 20 Hz to 2.0 MHz using an LCR meter (HP Model 4274 A, Hewlett-Packard, USA). For the measurement of electrical properties silver paste was coated on two extreme surfaces of the film to make them conducting.
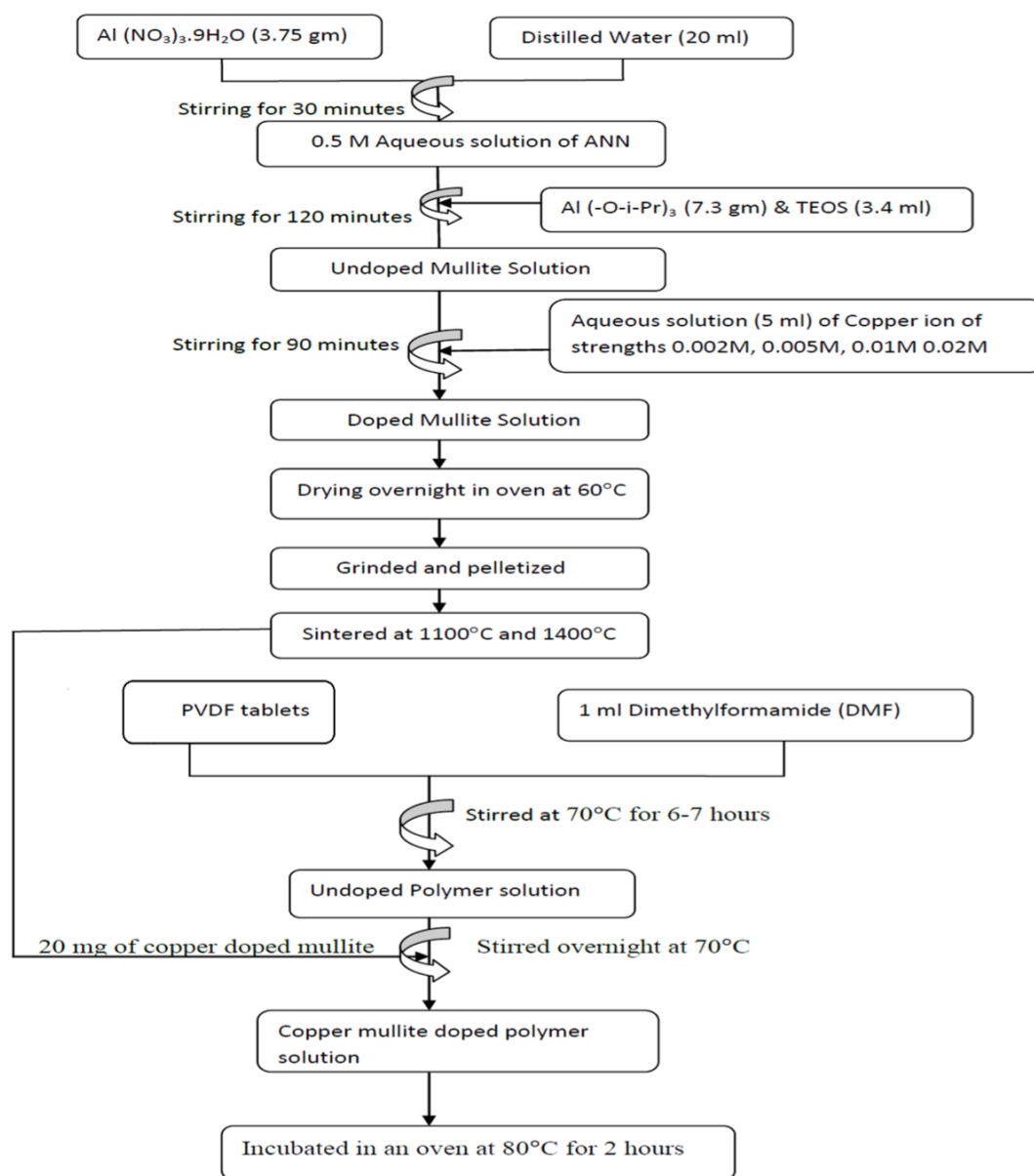
Figure 1: Flowchart depicting formation of copper ion doped mullite composite/polymer film.
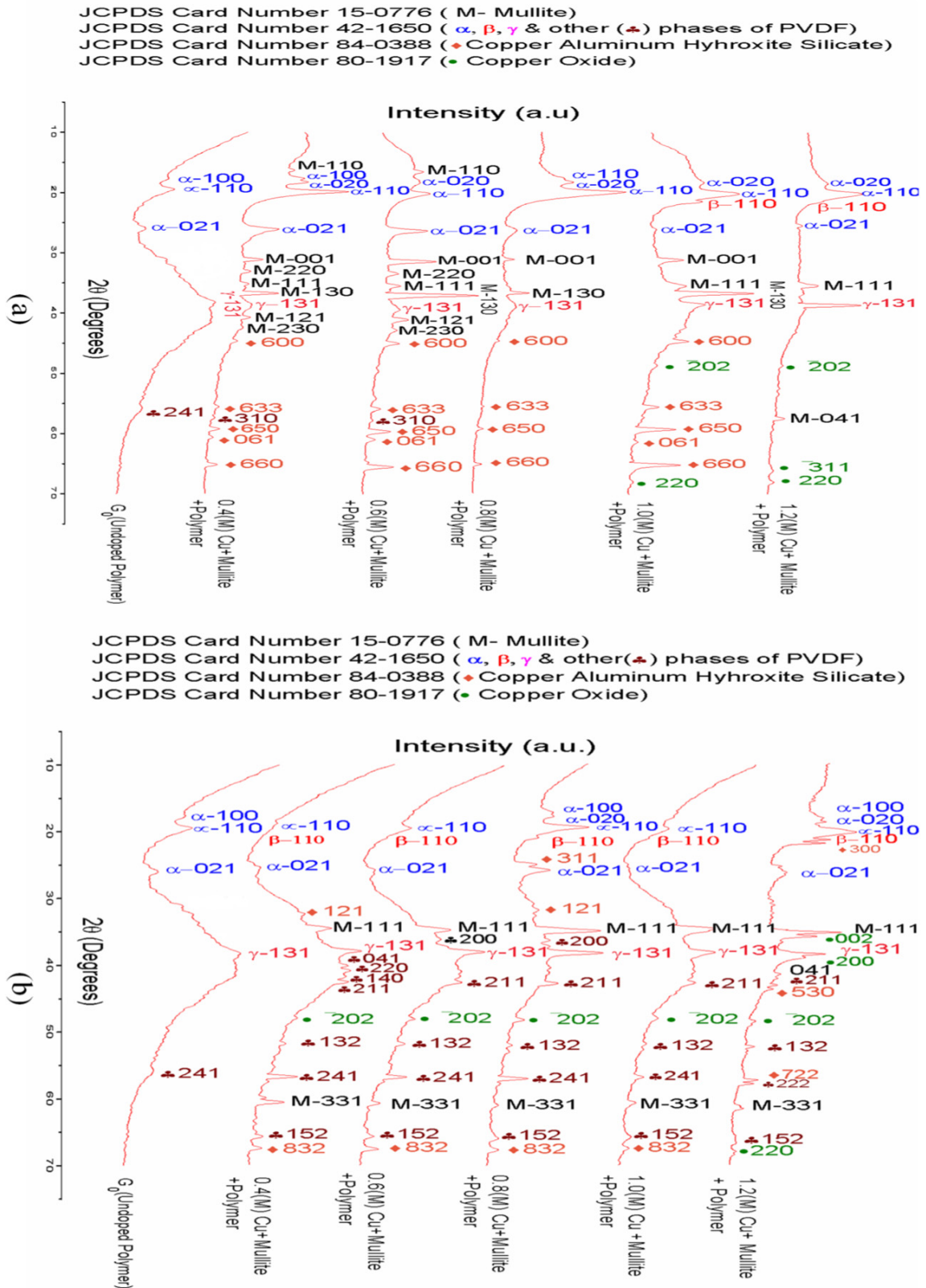
The morphology of the sintered gels was studied by Field Emission Scanning Electron Microscope (FESEM) (JSM 6700F, JEOL Ltd. Tokyo, Japan).

RESULTS AND DISCUSSIONS

X-Ray Diffraction Analysis

Figure **2** shows the X-ray diffraction pattern of PVDF thin films prepared at 70°C using DMF as a solvent. Undoped film (G_o) shows phases at $2\theta =$ 17.883(100), 20.135(110), 26.728(021), 38.657(131) and 56.877(241), where the first three peaks are the footprint of α phase, the peak at 38.657(131) confirms the presence of γ phase, and peak at 56.877(241) is an

additional phase of PVDF [23]. In case of other five composite films, where copper doped mullite composites were sintered at 1100°C (Figure **2a**) and 1400°C (Figure **2b**), all peaks of undoped films were obtained along with some extra phases of PVDF (JCPDS # 421650), Mullite (JCPDS # 421650), Copper aluminum hydroxide silicate (JCPDS # 84-0388) and Copper oxide (JCPDS # 80-1917). The peak at 20.8(110) is the evidence of β phase, and the peaks at 30.960(001), 33.228(220), 35.278(111), 36.993(130) and 57.561(041) indicates the existence of mullite in PVDF film [20, 24]. Concentration of copper ions has an overall positive effect on the growth of mullite phases. It can be seen that, in case of Figure **2a** β phase was visibly observed for only 1.0(M) and 1.2(M)

JCPDS Card Number 15-0776 (M- Mullite)
JCPDS Card Number 42-1650 (α, β, γ & other (♣) phases of PVDF)
JCPDS Card Number 84-0388 (♦ Copper Aluminum Hyhroxite Silicate)
JCPDS Card Number 80-1917 (• Copper Oxide)

JCPDS Card Number 15-0776 (M- Mullite)
JCPDS Card Number 42-1650 (α, β, γ & other(♣) phases of PVDF)
JCPDS Card Number 84-0388 (♦ Copper Aluminum Hyhroxite Silicate)
JCPDS Card Number 80-1917 (• Copper Oxide)

Figure 2: X-ray diffraction pattern of copper ion doped mullite composite/polymer film along with undoped polymer film, where mullite precursor gels sintered at (**a**) 1100°C and (**b**) 1400°C.

concentration of copper ion, but in Figure **2b** β phase is seen to be present from copper ion concentration of 0.4(M) up to 1.2 (M). From the diffractograms, it was found that with the increase of metal concentration (Cu^{2+}) in doped composite, phase transformation in composite increases. Interaction of metal ion doped

mullite with the polymer matrix is responsible for the accelerated transformation to polymer phases. Phase transformation was not only dependent upon the metal ion concentration, but also upon the sintering temperature. At 80°C, where the viscosity of the PVDF solution is comparatively low, the thermal energy is sufficient to rotate CF_2 dipoles which results in a motion of the neighboring CF_2 groups through the large scale trans(T)-gauche(G) conformational change. So, conformers aligned either in TTTT (β phase) or TTTGTTTG' (γ phase) form. Therefore, the solutions prepared using DMF solvent at 70°C produce polar PVDF films having α, β and γ phases [25].

FTIR Analysis

The FTIR spectra of copper ion doped mullite composite/polymer films in the range of 400-1500 cm^{-1} have been investigated in the transmittance modes shown in Figure **3**. Peaks at 490, 530, 612, 677, 763, 796, 970, 1076, 1210, 1383, and 1430 cm^{-1} are significant for α-phase identification [26, 27], where vibration bands at 530 cm^{-1} stands for CF2 bending, 612 and 763 cm^{-1} for CF2 bending and skeletal bending, and 970 cm^{-1} for CH2 rocking. The peaks at

510, 840 and 1275–1279 cm^{-1} are fingerprints of β-phase, where vibration bands at 510cm^{-1} are due to CF2 bending and 840 cm^{-1} due to CH2 rocking correspond to β-phase [28]. Peaks at 561, 741 and 900 cm^{-1} signifies the presence of mullite [20, 29]. These main PVDF characterizing peaks along with mullite peaks are present in all doped samples, indicating that the mullite is distributed among PVDF chains. The molecular vibration peaks of γ-phase are very close to β-phase. Therefore, it is very difficult to separate γ and β phase using FTIR spectroscopy.

The fraction of β-phase, F(β), can be calculated by the absorption peaks in the FTIR spectra by using the equation:

$$F(\beta) = \frac{X_\beta}{X_\beta + X_\alpha} = \frac{A_\beta}{1.26A_\beta + A_\alpha}$$

where, X_α and X_β are the crystalline mass fractions of α and β phase, and A_α and A_β are absorption band intensities for α phase and β phase, at wave numbers 763cm^{-1} and 840cm^{-1} respectively [16, 30]. The variation of F(β) with varying concentration of copper ion sintered at 1100°C and 1400°C is shown in Figure
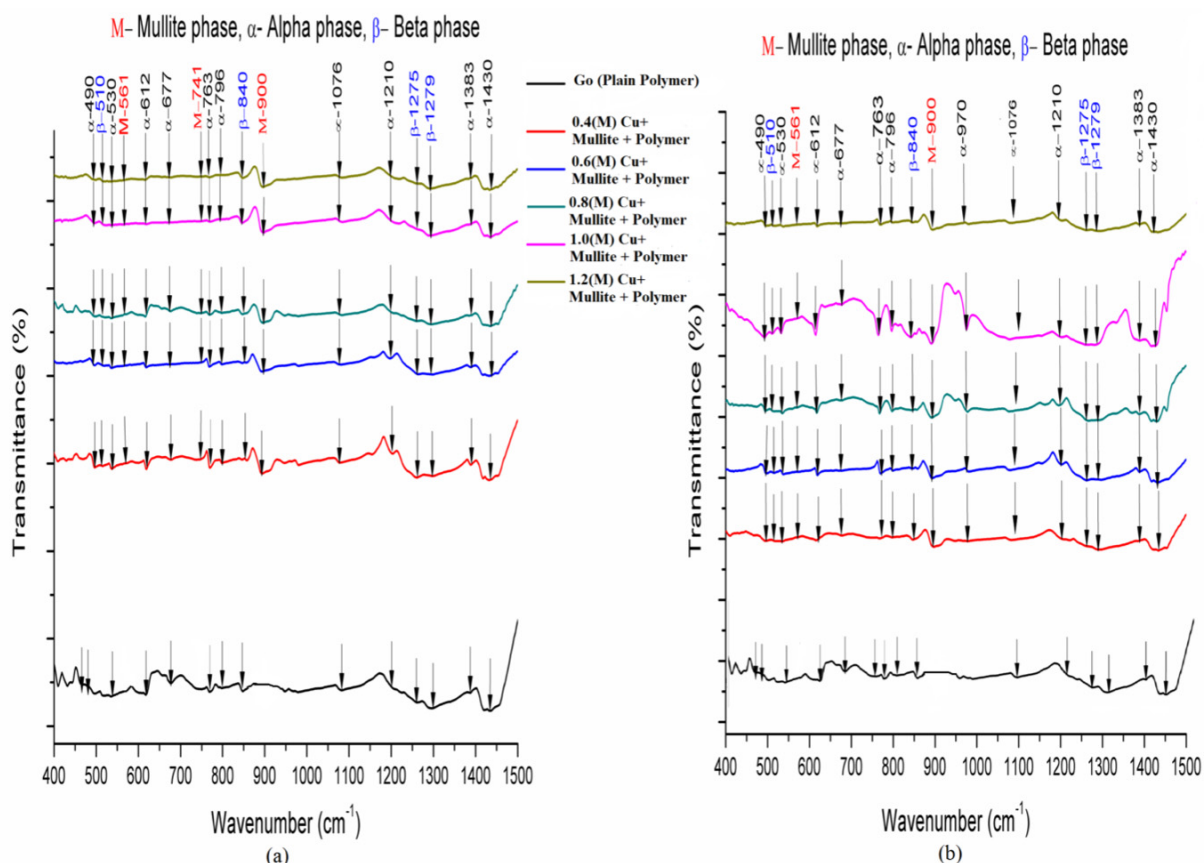
Figure 3: FTIR pattern of copper ion doped mullite composite/polymer film along with undoped polymer film, where mullite precursor gels sintered at (**a**) 1100°C and (**b**) 1400°C.
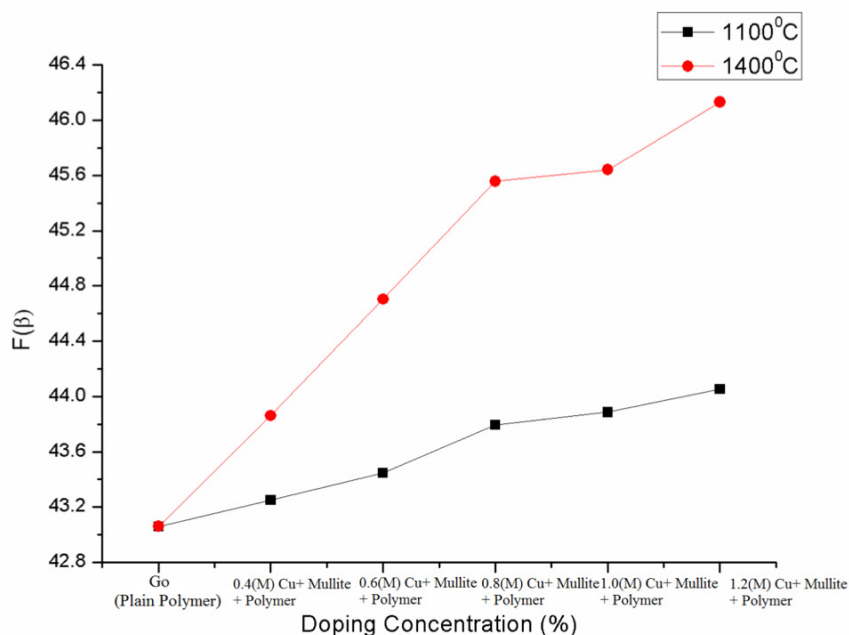
Figure 4: Fraction of β-phase (F(β)) with increasing concentration of doped mullite composite, where mullite precursor gels sintered at 1100°C and 1400°C.

4. It can be observed from Figure **4** that the addition of copper ion promotes β phase with respect to the undoped sample. The maximum amount of β phase is observed upon addition of 1.2(M) copper ion doped mullite when sintered at 1400°C into the polymer matrix.

Dielectric Study

Dielectric Constant

Dielectric measurement of each sample was performed at room temperature in the frequency range 1.0 KHz to 2.0 MHz. Figure **5** shows the variation in dielectric constant with increase in frequency. The plots clearly show that in both Figures **5a** and **5b**, dielectric constant increases with increasing concentration of copper doped mullite composite at the lower frequencies. Theoretically, dielectric behavior of ceramic-polymer systems can be explained qualitatively by permittivity of a composite to a combined dielectric effect of its individual constituents using Logarithmic mixing rule and free charge interruption with the interfaces of heterogeneous insulator/ conductor by Maxwell-Wagner-Sillar(MWS) polarization [31-34]. Good dispersion of copper doped mullite in polymer results in sudden improvement of dielectric properties at a particular frequency as during the procedure charges become entrapped in the interface between PVDF and doped mullite composite. A significant decrease in dielectric constant is observed with increasing frequency. From factual verifications

and observations, it has been noticed that for polar materials, initial value of dielectric permittivity is considerably higher, but on increasing the frequency the magnitude gradually drops; the main factor behind this behavior is that the dipoles are unable to follow the field variations at such high frequencies [17].

Dielectric value became 6.58 &19.96 at 1.0 KHz frequency, for 1.2(M) concentration of doped composite, sintered at 1100°C and 1400°C respectively which are 2.13 & 6.46 times higher than that of neat PVDF.
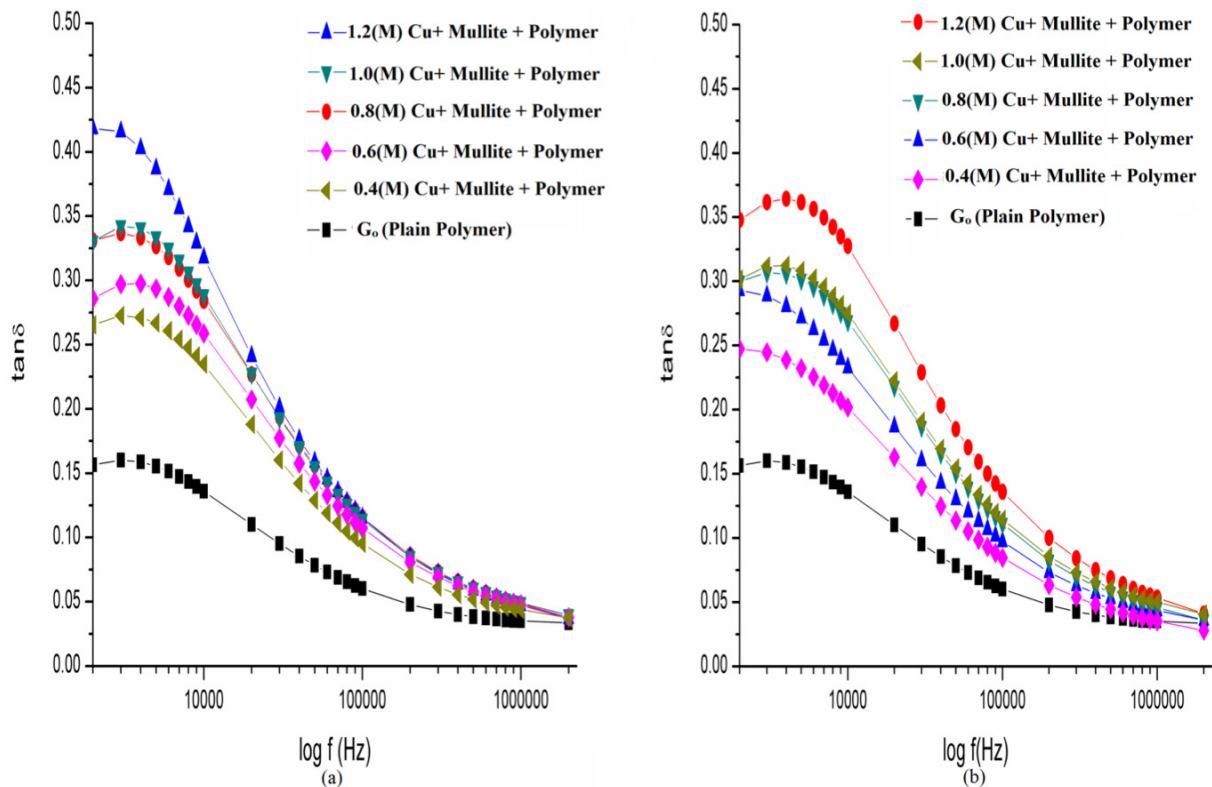
Dielectric Loss

Figure **6** shows the variation of dissipation factor (tan δ) with frequency in the frequency range 1.0 KHz to 2.0 MHz at room temperature. It shows a distinct enhancement in dielectric loss with increasing amount of copper doped mullite composite/ PVDF films. With the gradual increase of doping amount more interfacial areas are created and PVDF polymer chains are separated into smaller domains by the increasing conductive network.

Thus, more molecules or dipoles can rotate, leading to more active movement and more energy dissipation. As we know that dielectric loss is a measurement of energy dissipation from the movement or rotation of the molecules in the alternative electric field, therefore, as the amount of doped composite increased, even more interfacial area and smaller or thinner domains of
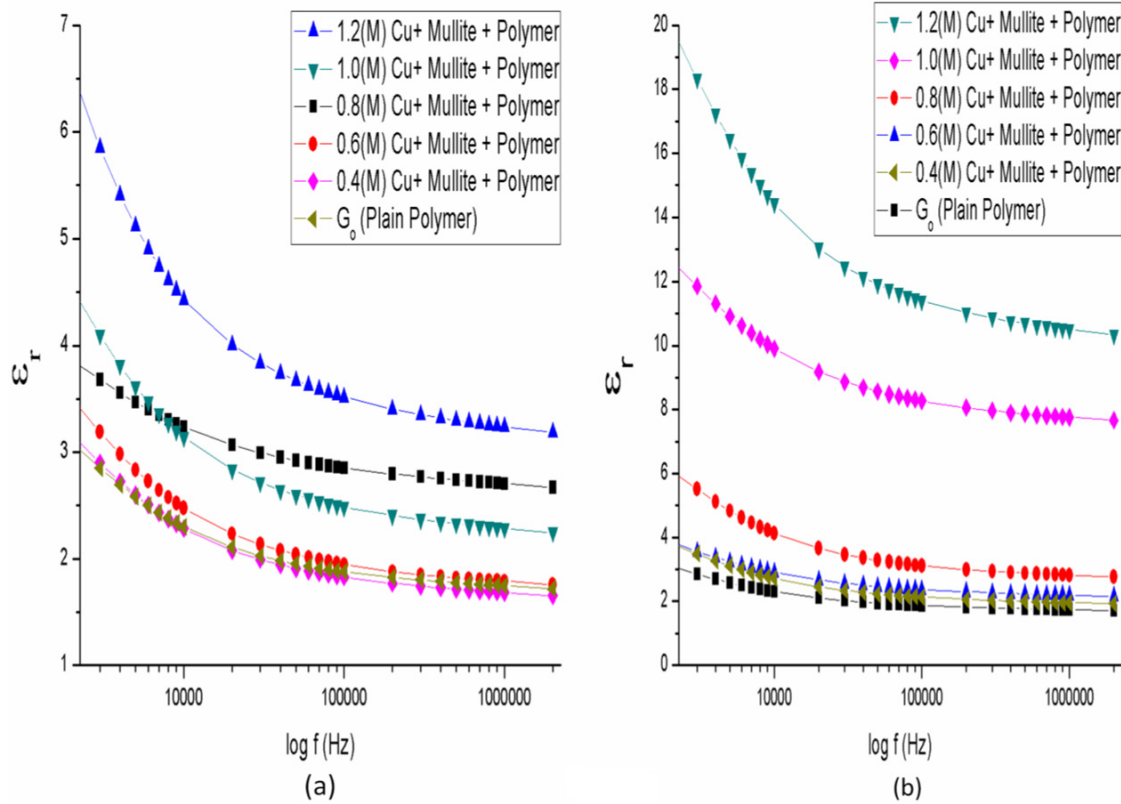
Figure 5: Frequency response of dielectric constant value (ε_r) of copper ion doped mullite composite/polymer film along with undoped polymer film, where mullite precursor gels sintered at (**a**) 1100°C and (**b**) 1400°C.

Figure 6: Frequency response of dielectric loss tangent (tan δ) of copper ion doped mullite composite/polymer film along with undoped polymer film, where mullite precursor gels sintered at (**a**) 1100°C and (**b**) 1400°C.
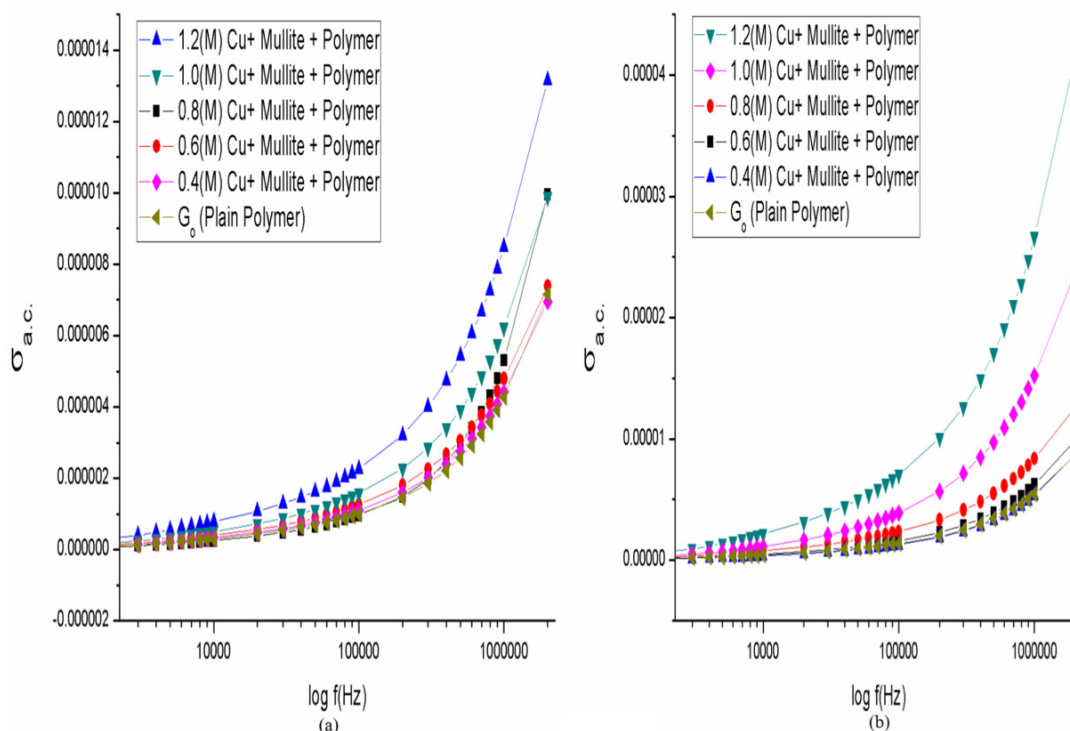
Figure 7: Frequency response of A.C. conductivity value ($\sigma_{a.c.}$) of copper ion doped mullite composite/polymer film along with undoped polymer film, where mullite precursor gels sintered at (**a**) 1100°C and (**b**) 1400°C.

PVDF polymer chain could be observed. Consequently, the enhanced movement of PVDF molecules may induce dielectric loss [24, 31, 35].

Electrical Study

A.C. Conductivity Analysis

The A.C. conductivity response with frequency range between 1.0 KHz to 2.0 MHz at room temperature is shown in Figure **7**. The A.C. conductivity has typical frequency dependence for all the samples, including pure PVDF which was found to increase with the increase in doping in the doped composite.

Electrical conductivity (σ_{total} (ω)) consists of two parts: A.C. conductivity ($\sigma_{a.c.}(\omega)$) and D.C. conductivity ($\sigma_{d.c.}$). The frequency of the electric field varies during A.C. conductivity whereas it remains constantin case of D.C. conductivity. $\sigma_{d.c.}$ depends strongly on temperature and dominates at lower frequency and higher temperatures, where, $\sigma_{a.c.}(\omega)$ has a dependence on temperature and dominates at higher frequency and lower temperatures. The relation for frequency dependent ac conductivity is

$$\sigma_{a.c.}(\omega) = A\omega^s,$$

where, A is constant, S is a function of temperature, value of which lies between 0 and 1 [15, 36].

The A.C. conductivity increases with increase in frequency, and the response is better for the samples sintered at 1400°C as temperature is the common response of polar polymer. As the temperature increases, the polymer becomes soft and the main chain segments become mobile as well as facilitating easier rotation of side chains. Thus, at higher temperatures more and more dipoles are oriented resulting in higher equivalent surface charge density, i.e., the conductivity increases [37] with increase in temperature.

Resistivity Analysis

For heat sink and electrical contact applications, thermal conductivity is the most important property, but this property is not easy to measure due to large experimental errors. Here, resistivity was selected in this study asit is easy to measure and can be translated into thermal conductivity *via* Wiedmann–Frantz equation:

$$\gamma/\sigma = LT$$

where, γ is thermal conductivity, σiselectrical conductivity, L is Lorenz number, which is constant for all metals (2×10^{-8} WΩK^{-2}) and T is absolute temperature [34]. Figures **8a** and **8b** shows an abrupt drop of resistivity up to 10 KHz, and then the rate of fall
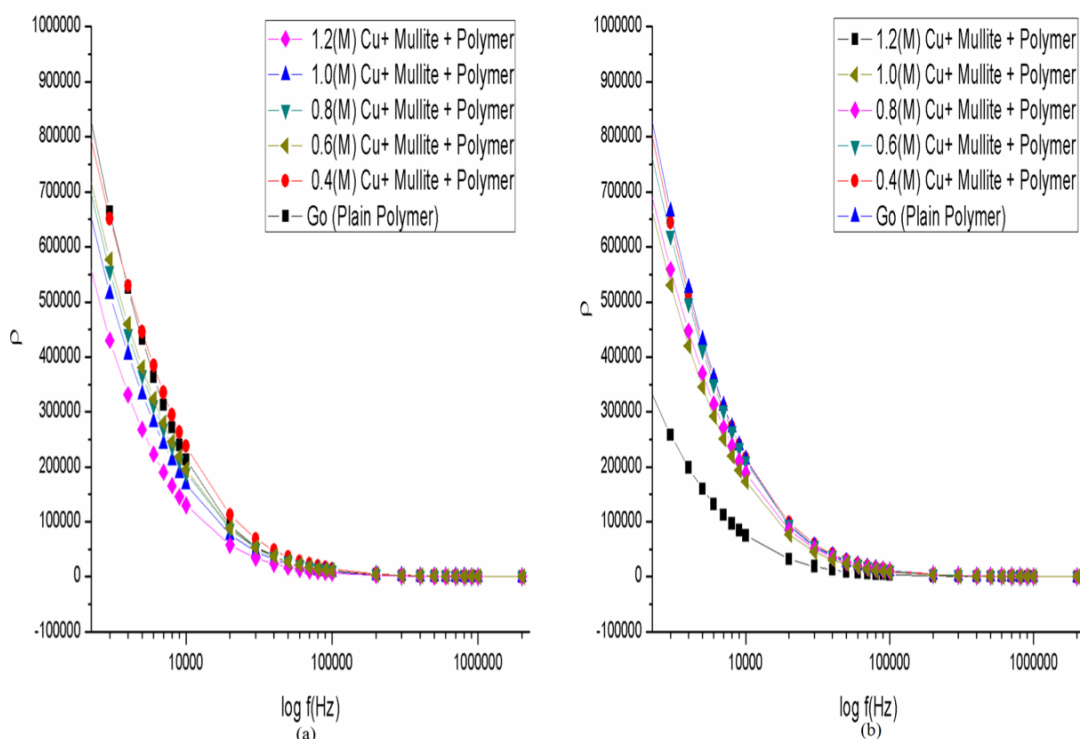
Figure 8: Frequency response of resistivity (Ω-cm) of copper ion doped mullite composite/polymer film along with undoped polymer film, where mullite precursor gels sintered at (**a**) 1100°C and (**b**) 1400°C.

Table 1:   Parameters Obtained from Dielectric, Electrical and Resistivity Analyses of Copper Ion Doped Mullite Composite/Polymer Film along with Undoped Polymer Film, where Mullite Precursor Gels Sintered at 1100°C and 1400°C

Sintering Temperature of doped mullite composite	Specimen	Dielectric Constant (ε_r)	Dielectric Loss (tan δ)	A.C. Conductivity ($\sigma_{a.c.}$)	Resistivity (Ω-cm)
	Undoped Polymer (G_0)	**3.09168**	**0.1564**	**$6.71343E^{-8}$**	**891246**
1100°C	0.4(M) Cu+Mullite +Polymer	3.17016	0.26531	$9.12112E^{-8}$	863017
	0.6(M) Cu+Mullite +Polymer	3.51633	0.28584	$1.00765E^{-7}$	816789
	0.8(M) Cu+Mullite +Polymer	3.86007	0.33021	$1.29436E^{-7}$	741503
	1.0(M) Cu+Mullite +Polymer	4.54428	0.33103	$1.66866E^{-7}$	717299
	1.2(M) Cu+Mullite +Polymer	6.58166	0.41822	$3.06088E^{-7}$	360567
1400°C	0.4(M) Cu+Mullite +Polymer	3.80529	0.24729	$1.25878 E^{-7}$	851692
	0.6(M) Cu+Mullite +Polymer	3.86400	0.29296	$1.27675E^{-7}$	771139
	0.8(M) Cu+Mullite +Polymer	6.10609	0.29990	$2.36208E^{-7}$	754254
	1.0(M) Cu+Mullite +Polymer	12.67614	0.30173	$3.48571E^{-7}$	706837
	1.2(M) Cu+Mullite +Polymer	19.96936	0.34788	$6.65954E^{-7}$	608268

in resistivity becomes lower. The drop in resistivity with frequency indicates the presence of glassy phase /amorphous phase in the mullite structure that may increase the mobility of the copper ion (Cu^{2+}), which finds an easy path to move and hence increases the electrical conductivity, keeping in mind that incorporation of transition metals in the periodic lattice of the mullite crystal structure helps in attaining a lower band structure [38].

Parameters obtained from dielectric, electrical and resistivity analyses are shown in Table **1**.

FESEM Analysis

Figures **9** and **10** shows upper surface (a), fractured surface (b) along with their corresponding EDAX images (c) of doped mullite composite/polymer films with 1.2M concentration of copper doped mullite sintered at 1100°C and 1400°C respectively.
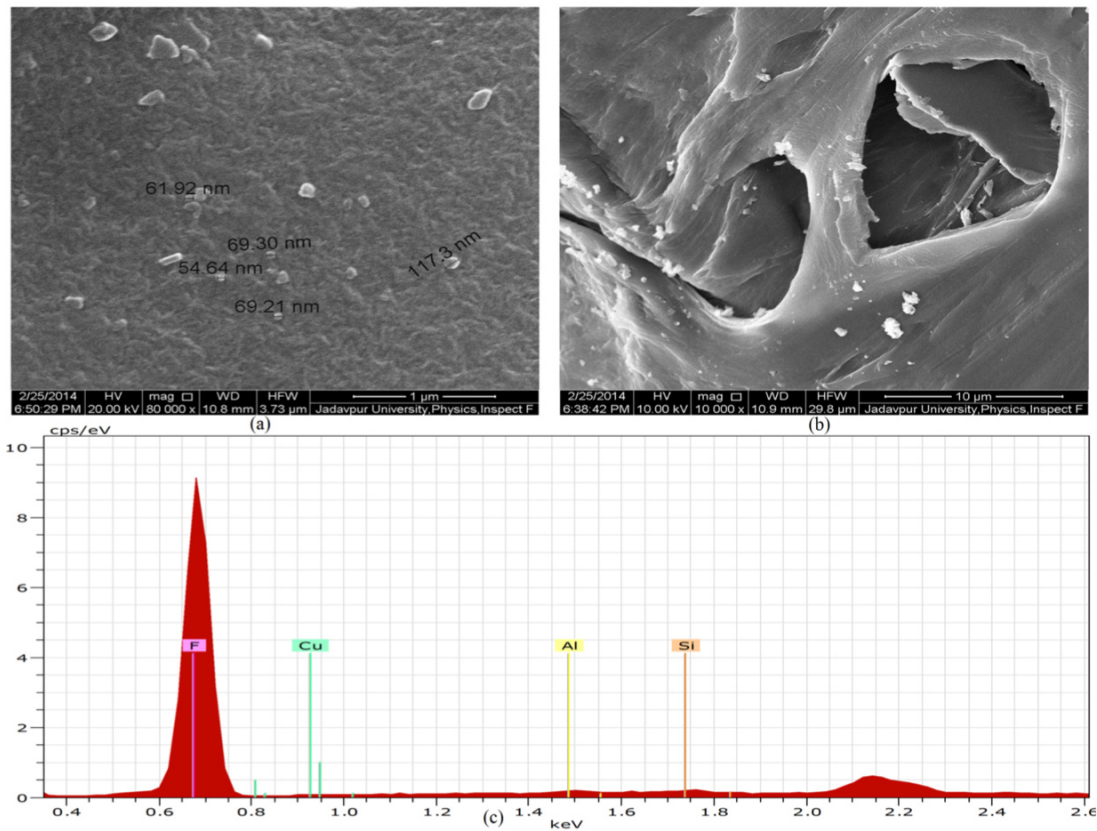
Figure 9: SEM images of upper surface (**a**), fractured surface (**b**) along with corresponding EDAX image (**c**) of doped mullite composite/polymer film with 1.2(M) concentration of copper doped mullite sintered at 1100°C.
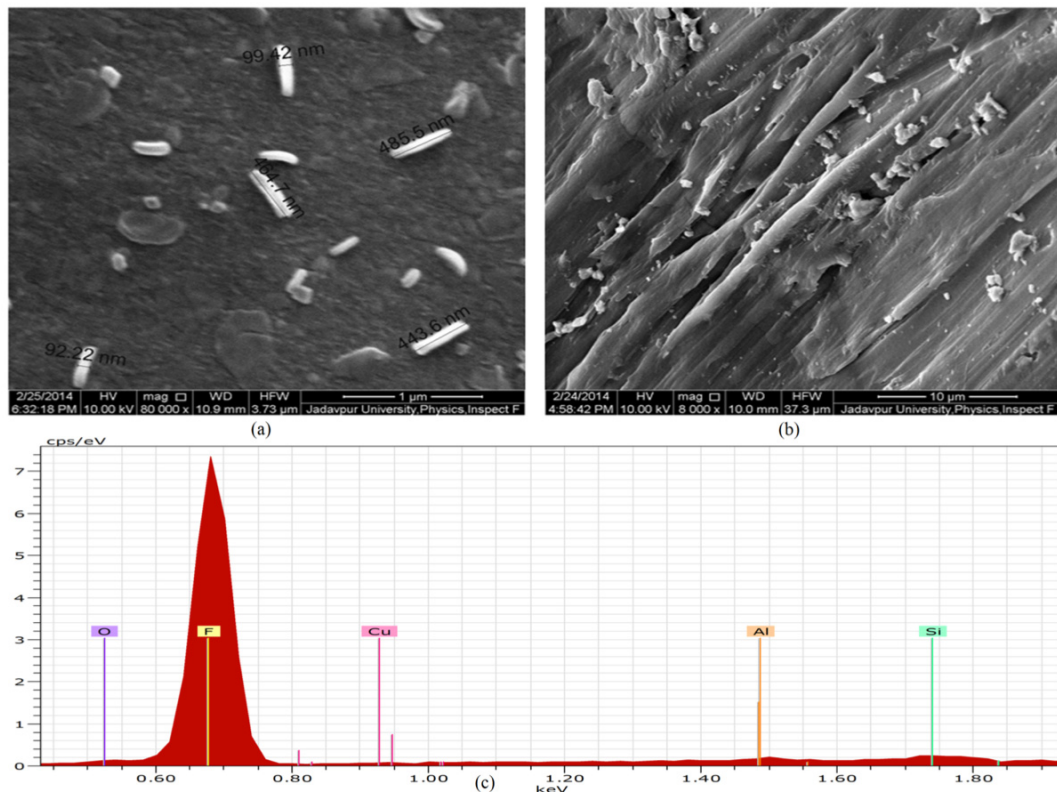
Figure 10: SEM images of upper surface (**a**), fractured surface (**b**) along with corresponding EDAX image (**c**) of doped mullite composite/polymer film with 1.2(M) concentration of copper doped mullite sintered at 1400°C.

Table 2: Parameters Obtained from EDAX Study with their Weight Percentages for 1.2 M Copper Ion Doped Mullite Composite/Polymer Film Sintered at 1100°C

Element	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Compound norm.	Comp. C [wt.%]	Error (3 Sigma) [wt.%]
Fluorine	93.08	93.00	95.49		93.00	35.09
Aluminium	1.03	1.03	0.75	Al_2O_3	1.95	0.36
Silicon	0.77	0.77	0.54	SiO_2	1.65	0.27
Copper	3.40	3.40	1.04		3.40	0.80
Oxygen	1.80	1.80	2.19		0.00	0.61
Total:	100.08	100.00	100.00			

Table 3: Parameters Obtained from EDAX Study with their Weight Percentages for 1.2 M Copper Ion Doped Mullite Composite/Polymer Film Sintered at 1400°C

Element	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Compound norm.	Comp. C [wt.%]	Error (3 Sigma) [wt.%]
Fluorine	89.63	91.34	93.76		91.34	34.88
Oxygen	2.71	2.76	3.36		0.00	0.89
Copper	3.15	3.21	0.99		3.21	0.81
Aluminium	1.18	1.20	0.87	Al_2O_3	2.27	0.40
Silicon	1.45	1.48	1.03	SiO_2	3.17	0.39
Total:	98.13	100.00	100.00			

It can be observed from the micrographs that, in case of copper doped mullite fired at 1100°C (Figure **9a**), the spherical mullite particles are embedded in the polymer matrix, whereas, in case of Figure **10a**, maximum number of needle shaped mullite particles takes place. Figures **9b** and **10b** are the evidences of doping, where images have been taken from the fractured field of the polymer. It can be clearly concluded from these images that, particles are doped in a well manner inside polymer matrix, which in turn affects its phase and electrical behavior.

The EDAX images (Figures **9c** and **10c**) confirm the presence of copper ion into polymeric system. Also the presence of Al & Si is the evidence of presence of mullite into polymer matrix. Elements obtained from EDAX study with their weight percentages are shown in Tables **2** and **3**.

CONCLUSION

In this research work, the ceramic–polymer composites are investigated due to some important physical properties such as high dielectric constant, low dielectric loss, and high-energy storage density. Phase changes in polymer film have been observed, which were due to the contribution of copper doped mullite composite, evident from XRD, FTIR spectroscopy and FESEM characterizations. Within the frequency range studied, the role of doped mullite composite on polymer matrixwas found to enhance its electrical properties compared to that of pure polymer. The composite film showed maximum dielectric constant value of 19.96 at 1.0 KHz for 1.2(M) copper doped mullite inside polymer matrix sintered at1400°C. The dielectric constant of the composites studied follows the logarithmic mixing rule and Maxwell-Wagner-Sillars (MWS) polarization theorem. A.C. conductivity increased with frequency and was found to depend on the amount of glassy phase and concentration of mobile ions present in the composites. With the increase in concentration of doped ceramic composite its resistivity was found to decrease. Moreover, it can be concluded that copper ion doped mullite composite has a positive impact on the polymer matrix, as it helps to change its phase behaviour, microstructure and increases electrical conductivity, which have potential application in many fields such as embedded capacitors, sensors, gate dielectrics, and electric energy storage devices applied in the electronics and electrical industry.

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