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Raman and Florescence Spectra of Lead-Copper Oxide Doped PMMA Films

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Abstract: In this work we present the synthesis of Lead Copper Oxide (PbCuO) nano-powder via sol-gel method using respective metal chlorides as precursors; and insertion of these nano-particles as dopant in poly-methyl-methacyrlate (PMMA) solution to prepare PbCuO-PMMA composite film using the solution cast method . The structural analysis of the prepared PbCuO nanopowder and PbCuO doped PMMA film has been carried out by XRD, FESEM, FTIR and florescence Spectroscopy. From XRD studies the crystalline size of PbCuO nanoparticles is found to be around 45 nm estimated from Scherrer formula. FTIR studies revealed that nanopowder shows vibration of prepared material and well mixed in polymer. FESEM measurement shows that particles are in almost irregular shape and some nanorod like structures are obtained. The effect of insertion of the lead-copper oxide nanoparticles on FL properties of poly(methylmetha)crylate has been also studied using from florescence spectra, it is seen that the intensity of emission as-well-as emission peak wavelength changes with solvent.

Keywords: PMMA, mixed metal oxides, PbCuO, Florescence spectra, Raman spectra.

I. INTRODUCTION

Poly (methylmethacrylate) (PMMA) has been the most favored polymer to be experimented for mixing, co-polymerizing or insertion of nano-fillers via fabric scientists because it now not most effective reveals fascinating properties of being obvious and light weight but is also tremendously compatible with most natural and inorganic materials. PMMA also own top tensile power, insulating properties, ease of managing and processing. A speedy look on the literature shows that due to presence of every other organic/inorganic material even in small portions within the PMMA long chain molecule; appreciably changes its optical [1-6], electrical [7-12], mechanical [13-14] or thermal properties [17]. Lead-copper oxide nanoparticles are of interest as they have got giant potential to be used in kind of programs, along with optical coatings, laser diodes and catalysts, subject impact transistors, area emission arrays, ultraviolet lasers, mild emitting diode, sensors, biosensors, catalyst, electricity garage and sun cells [15]. Several techniques which include hydrothermal, sol-gel, electrochemical deposition, microwave, sono chemical have been followed for formation of Pb-CuO nano-powders [22]. We've used the easy sol-gel method. The approach consists of dissolution of metallic-ion precursors (metal chlorides) in a suitable solvent and obtaining gel. So to analyze how the combined metal oxide might affect the structural and fluorescence properties of PMMA we concept of incorporating Lead copper oxide in PMMA. In the present research, we record the synthesis of Lead Copper oxide nano powder the usage of the sol-gel technique and preparation of films by using putting this nano-powder into PMMA and the analysis of the investigated structural and florescence properties of those prepared sample films. The particular synthetic procedure and characterization of pure and composite PMMA films are stated right here.

II. EXPERIMENTAL WORK

1) *Chemical Involved:* Lead chloride ($PbCl_2$), copper chloride ($CuCl_2$) and dichloromethane of analytical grade were purchased from Merck Specialties Pvt. Ltd, Mumbai; PMMA granules were purchased from M/s Gadra Chemicals Bharuch; hydrochloric acid (HCl) and ethyl alcohol (C_2H_5OH) were purchased from Himedia Laboratories, Mumbai. All these chemicals were used without further purification.
2) *Synthesis of Lead-Copper Oxide Nano-Particles by sol-gel Technique:* Pb–CuO nano-structures were synthesized using the sol-gel method. The precursors, 4 gm of white anhydrous in different beakers and 10 gm Lead chloride of blue copper chloride were first grinded for 20 minutes using mortar and pestle into fine powder and then were kept in a beaker. Then 20ml of dilute hydrochloric acid was gradually poured into this mixture contained in the beaker kept on a magnetic stirrer for a continuous stirring. After an hour when the mixture dissolved in the acid, we added ethanol (purity99%) drop-wise into the beaker and the temperature was increased to 60°C to form sol. The reaction produced a solution of yellowish colour with a tinge of blue. We kept it stirring for another four hours at room temperature while the whole mixture got dissolved in ethanol during this process. The precursors react with OH group of ethanol likewise

$$CuCl_2+PbCl_2+2HCl+3C_2H_5OH \xrightarrow[\text{Dry ether or Hcl}]{\text{ZnCl2(anhy.)}} [Pb\text{-}O\text{-}Cu] + 3C_2H_6\uparrow + 6Cl\uparrow$$

The $ZnCl_2$ in the above reaction is anhydrous in nature and is the *Lucas reagent* that acts like a basic reactia.

After this we left the solution to cool down, within several minutes, a reaction occurred showing a rapid formation of a rigid bluish green colored gel. Then the gel was dried at the same temperature. To remove residual impurities, the final product was washed several times with deionized water and ethanol. Obtained gel was dried at 80°C for an hour in an oven to obtain Pb-CuO nanopowder.

Figure 1**:** Prepared Pb-CuO sol gel product.

3) *Synthesis of pure and Pb-CuO doped PMMA Films:* We took two beakers of 100ml and in each a fixed amount of 1gm granule PMMA crystals were made to dissolve in 20ml dichloromethane and 5 ml of ethyl alcohol that acts as solvent. The molten PMMA is stirred uniformly in an ultra-sonicator for 6 hrs at room temperature to assure the homogenous dispersion of polymer particles without concentricity throughout the solvent. After this, solution of one of the beaker was poured into a glass flat bottom petri dish of diameter 6 cm. The solution spread uniformly in all direction in the petri dish as it was kept floating freely over a pool of mercury so as to achieve perfect leveling and uniformity in the thickness of the film. Then we added 100 mg of Lead-copper oxide nano-particles into the solution of another two beaker and allowed this to stir on a magnetic stirrer for 18 hours. When the nano-particles got completely dissolved in to the PMMA solution, we poured this solution into another glass flat bottom petri dish kept floated over mercury. The solvent in both the petri dishes was allowed to disappear slowly at pervasive temperature under atmospheric pressure for almost twenty four hours. The dried samples from both the petri dish were then peeled off by tweezers clamp. We obtained transparent PMMA film and fluorescent green coloured Pb-CuO doped PMMA film of 120µm thickness as shown in figure 2. Now onwards we will refer the sample film of pure PMMA as P1 and that of Pb-CuO doped PMMA as PCOZ1 and PCOZ2. These films were then vacuum dried before proceeding for characterization.

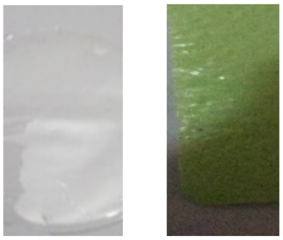

Figure 2**:** Prepared film of pure PMMA and Pb-CuO doped PMMA film of both ratio.

4) *Characterization:* The synthesized Pb-Cu oxide nano-particles and their doped PMMA films were characterized using X-ray diffractometer XRD (PANalytical unit using software X'Pert°Pro3) equipped with Cu-K_α radiation of wavelength□□ = 1.5406A° at accelerating voltage 30 kV. The corresponding ligand coordination and functional groups of powders and prepared films were analyzed by FTIR Perkin Elmer Spectrum Version 10.4.00 FTIR Spectrophotometer in the region 500-4000 cm^{-1}. The surface structure of the composite samples was investigated using S-3700N FESEM field emission scanning electron microscope. The florescence spectra was obtained using fluorescence emission spectroscopy

III. RESULTS AND DISCUSSION

A. X-Ray Diffraction Studies

In the available literature, the diffraction peaks of pure PbO have been indexed between 10° to 20°, and 50° to 60° [18-19]. Similarly the prominent peaks of CuO are indexed to a monoclinic phase at 2θ = 35.5°, 38.8°, 48.6° corresponding to (*hkl*) value of (100) (201) and (103) planes[19] matched with the JCPDS No 48–1548[15]. In the XRD data of the mixed metal oxide nano powder of Lead copper oxide, the copper peaks become dominant as seen in figure 3(a). The data has been depicted in the figure. The broad peaks witnessed in the diffraction pattern indicate the size of particles is of nanometer scale. We have also evaluated the average crystallite size of Pb-Cu oxide from the FWHM of the intense peaks using the Scherrer's equation; D=0.9λ/β cosθ, where λ is the wavelength of the incident radiation, D is the grain size, β is the experimentally observed diffraction peak width at full width at half-maximum intensity (FWHM) and θ is the Bragg angle. The average crystalline size of Pb-CuO nanoparticles from the intense peaks is found to be around 45.95 nm.

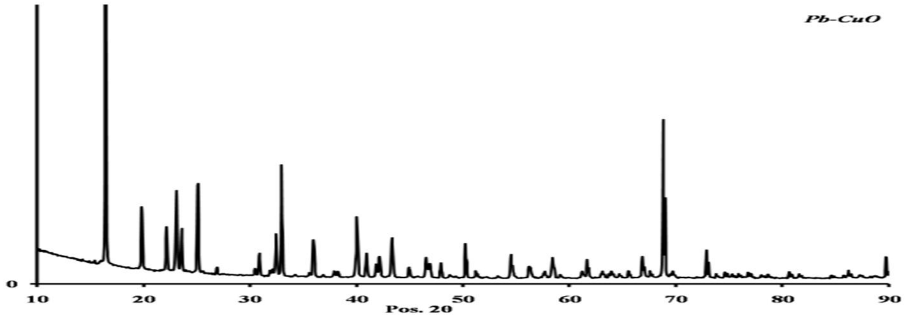

Figure 3(a)**:** XRD pattern obtained for Pb-CuO nano-powder

The XRD data for pure PMMA depicted in figure 3 (b) shows a predominant and broad peak with a maximum at 2θ = 13.89° along with broad but low intensity peaks at 30° and 34°. These broad peaks indicate the amorphous nature of the polymer. These are in good agreement with the reported ones [23].

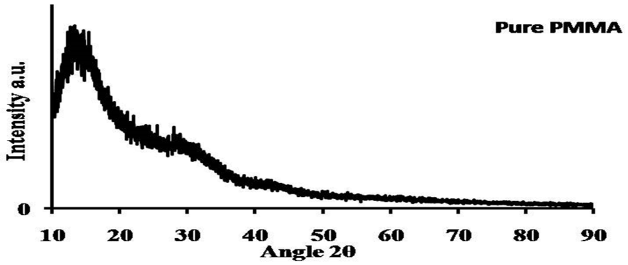

Figure 3(b)**:** XRD pattern obtained for pure PMMA film

The XRD pattern of PCZO film obtained on doping Pb-CuO nanoparticles into PMMA, clearly shows that there is a low broad peak at 13.8° of PMMA and sharp peaks at 31.7°, 34.4°, 36.2°, due to copper and peaks at 2θ =58.25°, along with low intensity peaks at due to lead oxide nanoparticles.

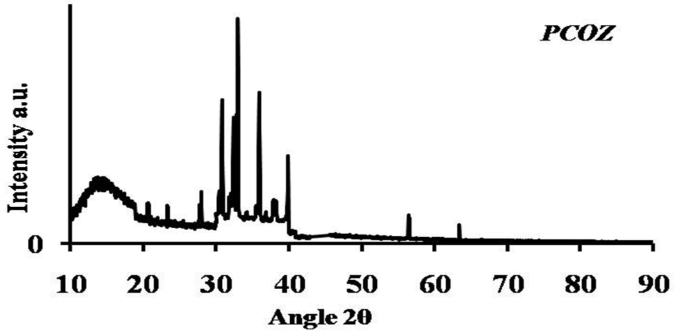

Figure 3(b)**:** XRD pattern obtained for Pb-CuO doped PMMA film

B. Analysis of SEM Images

SEM images of sol-gel product Pb-CuO nanoparticles, pure PMMA film and Pb-CuO doped PMMA film are given in figure 4. The Pb-CuO doped PMMA film possess smooth surface as compared to that for PMMA. The addition of mixed metal oxide has smoothened the rough fractured surface of pure PMMA.

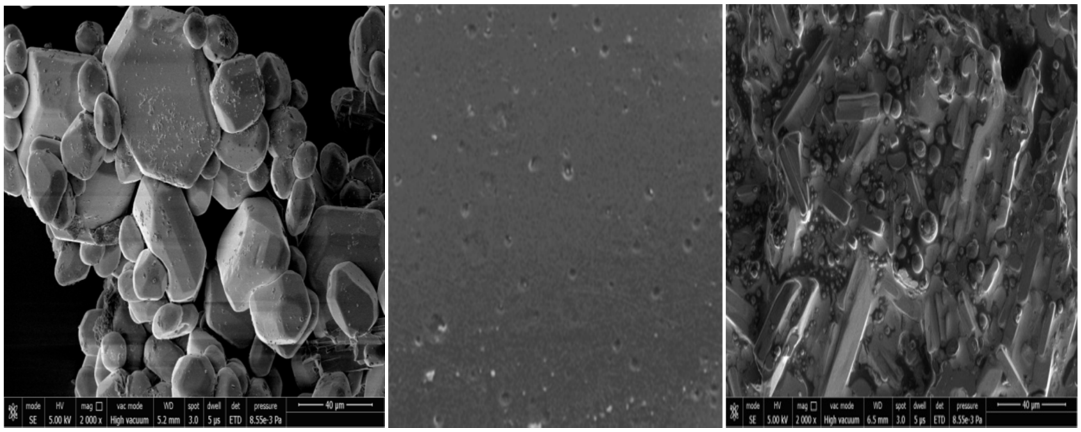

Figure 4: SEM images of Pb-CuO nano powder, PMMA and Pb-CuO doped PMMA film.

C. Analysis of FTIR Spectra

The FTIR data obtained for sol-gel product Pb-CuO is shown in figure 5(a). The prepared films of pure PMMA and Pb-CuO doped PMMA were cut into very small pieces for FTIR investigations and the obtained spectra are shown in figure5(b). The absorption peak at near 466.74 cm^{-1} indicates the presence of Pb-O Stretching and also the peak at near 557.39 cm-1 indicates the presence of oxides [19]. The characteristic peaks in these figures represent the vibrational modes of the molecules. In figure 5(a), the peak at 437 cm^{-1} is the characteristic absorption of Pb–O bond. The peaks observed in between 600 and 1050 cm−1 have strong absorption band due to stretching of Cu–O along the [−202] direction in monoclinic phase [20]. The peak observed at 2270 cm^{-1} is due to the presence of atmospheric CO_2 [20]. In region between 3000 to 3500 cm^{-1} due to srong O-H bond and hydrated CuO samples are responsible for the creation of peaks[17]. It is confirmed that the final product is the presence of lead and copper oxide.

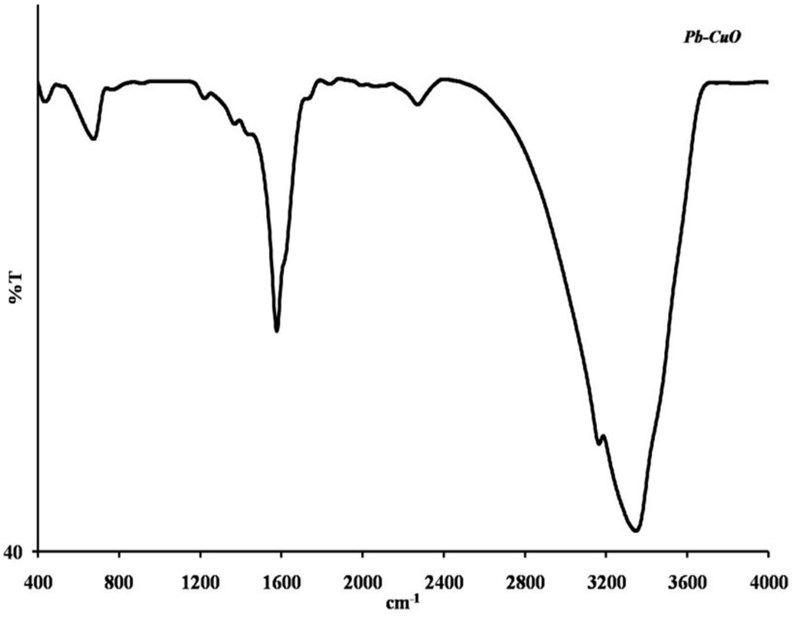

Figure 5(a): XRD pattern obtained for Pb-CuO powder

The modes obtained for the pure PMMA sample are listed in the Table 1 which is in good agreement with the reported ones [24].

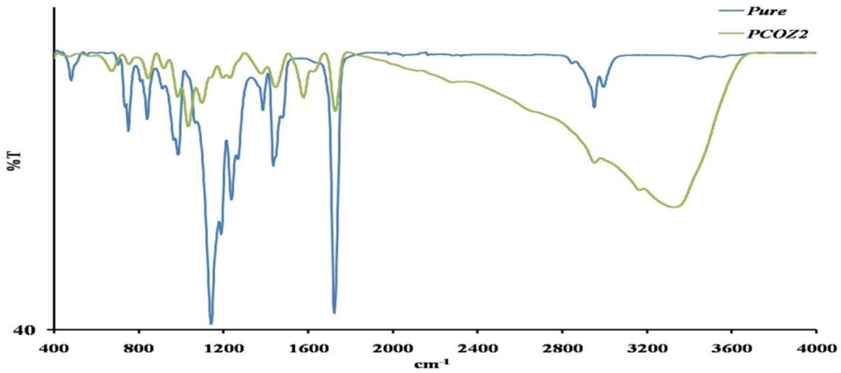

Figure 5(b)**:** FTIR Spectrum obtained for PMMA film and Pb-CuO doped PMMA film.

However with the incorporation of Pb-CuO in PMMA, we see appearance of all these peaks indicating the formation of the composite.

Wave number (cm^{-1})	Mode
751	C– C stretching bands
840	CH_2 rocking mode
986	CH_3-O rocking
1142	C-O anti symmetric stretching in C-O-C linkage
1189	CH_2wagging mode
1238	C-C-O symmetric stretching
1386	CH bending
1439	CH_3 bending
1724	C=O stretching mode
2950	C-H symmetrical stretching
2994	C-H asymmetrical stretching

Mode	Wave number (cm^{-1})
Pb-O bond	437
Cu-O	674
Arometic C-H	774
Arometic	1223
-O-CO-CH_3	1369
Arometic	1577
With strong intensity	1622
No information	1739
No information	2271
O-H bond	3162
O-H bomd	3332

Table 1: Vibration modes of PMMA and Pb-CuO-PMMA

D. Study of Florescence Properties

Photoluminescence is a popular spectroscopic technique to perform absorption studies on metal oxide particle systems. The excitation energies for these mixed metal oxides have been chosen on the basis of the most intense FL emission intensities. Figure 6(a) and (b) show the FL spectra at room temperature for the pure PMMA and Pb-CuO doped PMMA nano-composite films respectively.

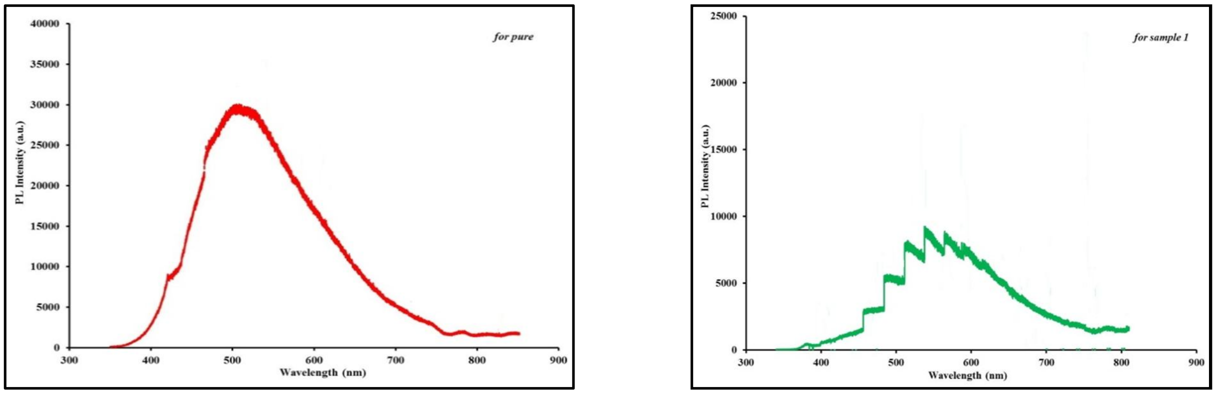

Figure 6: FL spectra of (a) Pure PMMA composite film (b) Lead-copper oxide nanoparticle doped composite film.

We can see that for the pure PMMA film there is only one broad visible emission centered at 510 nm with IR emission at 780 nm, while the PL spectra for Pb-CuO doped PMMA film shows emergence of visible emission peak at 465 nm and 510 nm, 520 nm, 545 nm and IR emission peak at 780 nm respectively. Further from literature it is known that emission peak at 545nm arises from the singly ionized oxygen vacancy resulting in green emission of CuO materials because of recombination of a photo generated hole with a singly ionized electron in valence band. The visible emission peak at 510 and 410 nm was originated from the excitonic recombination corresponding to that for PMMA [21]. Some new peaks are appearing due to presence of lead. The visible emission peaks have low intensity compared with that for pure PMMA.

E. Raman Spectra of Pb-CuO nano powder doped PMMA Composite Film

The Raman spectrum of the samples was measured using a STR5050 (500 nm-3000 nm) confocal micro Raman spectrometer. The diode pumped solid state (DPSS) laser of wavelength 532 nm was used as a source of excitation. Figure 7 depicts the Raman spectra of Pb-CuO-PMMA film. A careful literature survey points that “copper oxide has a Raman peak at almost 600 cm^{-1} [25]. Where as “lead oxide shows its peaks at almost 653,515, 424 cm^{-1} [26]. While PMMA has this characteristic peak between 2500-3500 cm^{-1}, which is shown in figure 7(a) [27]. Our results too are in agreement with the reported data. A quick glance of figures 7 reveals the dominance of the dopant materials as shown by peaks at 600 cm^{-1} for copper oxide and 450 cm^{-1} for lead oxide along with peak at 2700 cm^{-1} for PMMA.

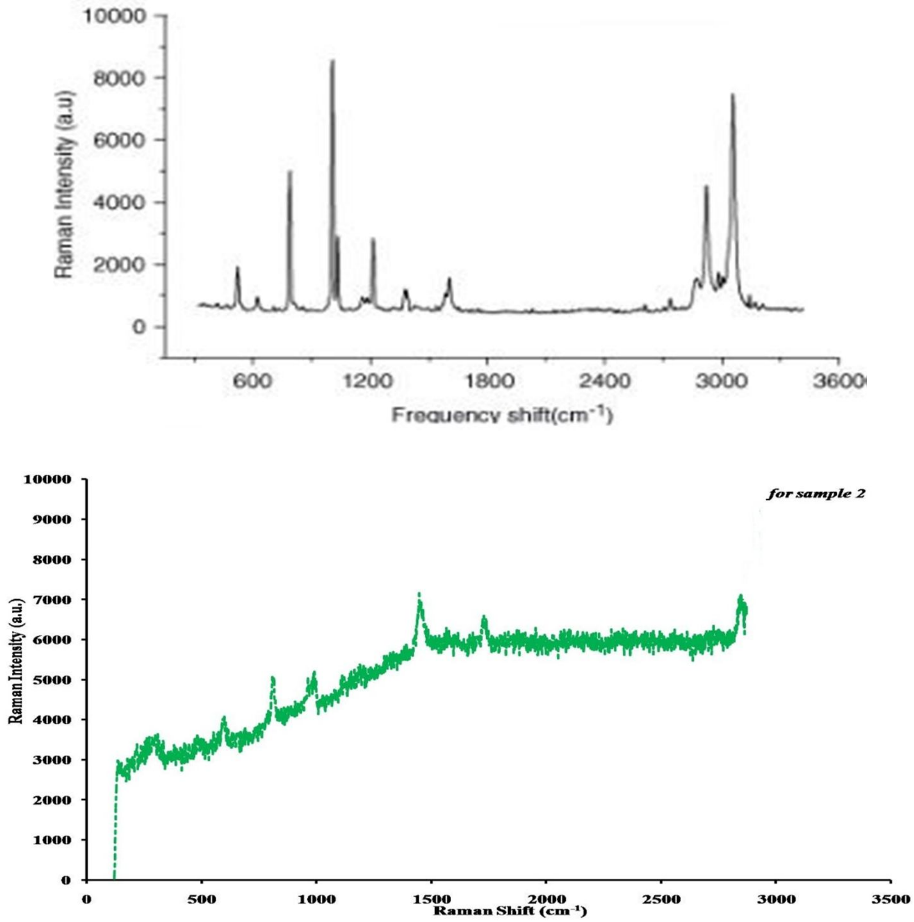

Figure 7 (a) Raman spectra of pure PMMA (b) Raman spectra of Pb-CuO-PMMA film.

IV. CONCLUSION

Here we have explained the experimental procedure to synthesize lead-copper oxide nano-powder through sol-gel process and insertion of it in PMMA to cast Pb-CuO-PMMA film. The XRD, FTIR and SEM pattern of such film shows that the metal particles get have well blended into the long chains of polymeric material and the florescence and raman spectra it is seen that the intensity of emission as-well-as emission peak wavelength changes with doping.

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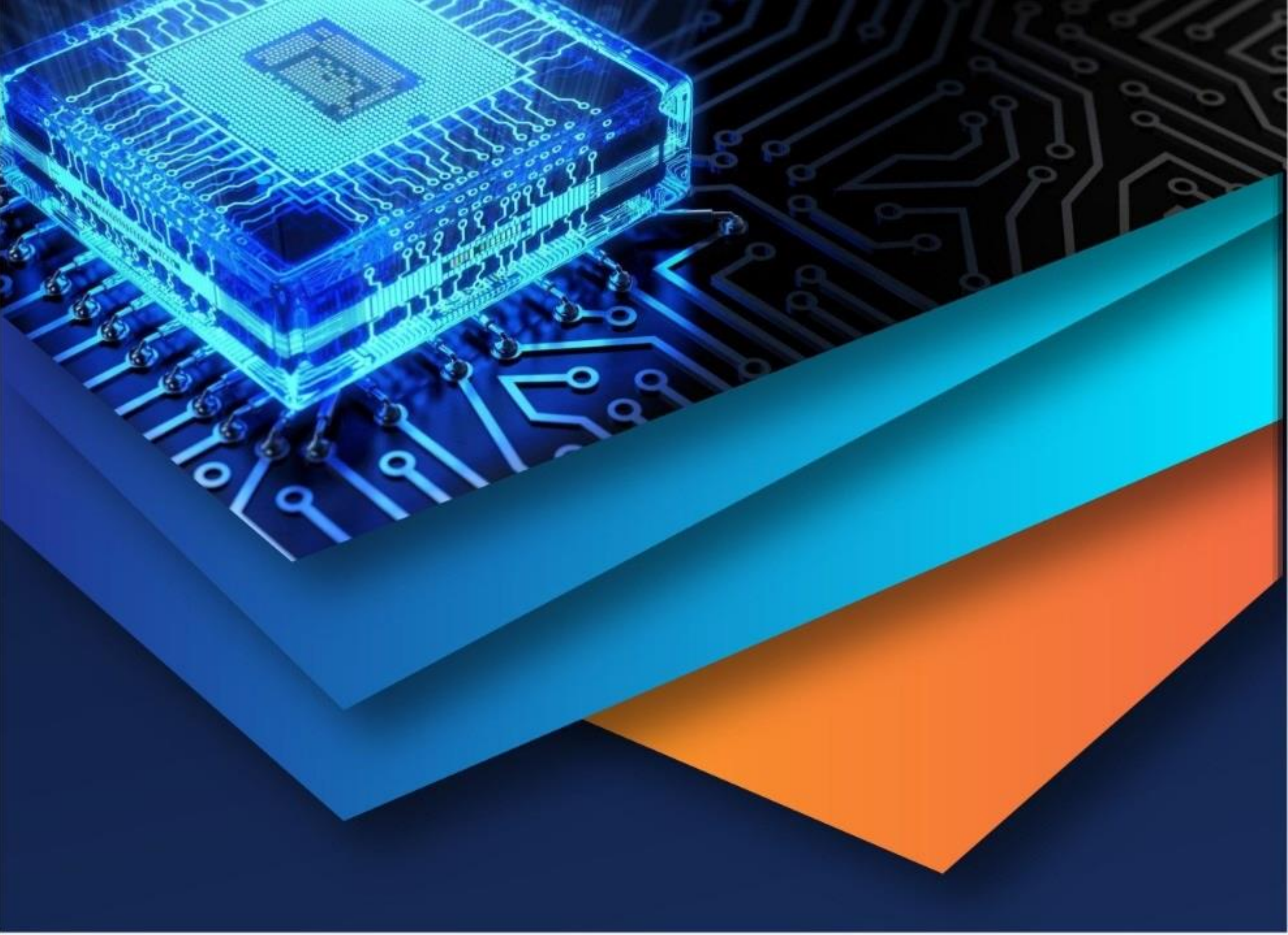

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