RJC

RASĀYAN *J. Chem.*
Vol. 12 | No. 3 |1085 - 1090| July - September | 2019
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

SPECTRAL CHARACTERIZATIONS OF Cu^{2+} IONS DOPED $CaZn_2 (PO_4)_2$ NANOPHOSPHOR

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ABSTRACT

Cu^{2+} ions doped $CaZn_2(PO_4)_2$ nanophosphor was prepared by solid-state reaction (SSR) method. The synthesized material was studied by different characterization techniques like X-ray diffraction, Fourier Transform Infra Red, optical absorption and Electron Paramagnetic Resonance (EPR) techniques. The diffraction pattern exhibited the prepared sample belongs to the triclinic crystal structure and average grain size of the crystalline sample was determined as 82 nm. From the EPR spectrum, the bonding parameter and the calculated values of spin-Hamiltonian parameters suggest that Cu^{2+} ions have rhombically distorted octahedral site symmetry. Absorption spectrum contains four bands observed at 689, 830, 1050, and 1207 nm which are due to the transitions $^2A_1(d_{x^2-y^2}) \rightarrow {}^2B_2(d_{yz})$, $^2B_1(d_{xz})$, $^2A_1(d_{xy})$ and $^2A_1(d_z^2)$ respectively. The Fourier transformed infra red spectrum exhibited fundamental vibration frequencies of Phosphate (PO_4^{3-}) ions along with other functional groups.

Keywords: Calcium Zinc Phosphate, EPR, Coating Materials, Pigments, Optical Absorption.

INTRODUCTION

Synthesis of inorganic phosphate nanopowder is a quite interesting developing area of research over the past few decades. Phosphate is a chemical derivative of phosphoric acid in inorganic chemistry. Generally, phosphates are used in processed foods, pharmaceutical products, metal polishes, water-based paints, coatings, in the treatment of potable (drinking) water in addition to cleaning products. Owing to their diversity of applications of these phosphates as fluorescent materials, dielectric substances, dental cement, prosthetics, fuel cells and pigments, phosphates have drawn the attention of many research groups.[1-3] They are also used in catalysis, ion exchangers and in low thermal expansion ceramic materials.[4-6] Among the phosphates, zinc phosphate is a white non-toxic pigment with anti-corrosion characteristics and adhesion capability. It is also used as a chemically bonded ceramic material (CBC) and also serves as an excellent flame retardant. It is suggested as the first bioceramic in dental applications.[7] Phosphate based inorganic nanoparticles like Zinc phosphate has low activity owing to their weaker solubility and hydrolysis. Zinc phosphate has been modified by adding cations such as Ca^{2+} ion to improve its activity.[8] Calcium Zinc Phosphate is an inorganic phosphate material prepared by several routes. [8-12] Among the various methods, Solid state reaction method is very convenient due to easy preparation, low cost, chemical & thermal stabilities and less environmental impact. Calcium Zinc Phosphate (CZP) nanopowder was first prepared by Ding and Wang with better anti-corrosion properties.[9] CZP finds a lot of applications particularly in the coating industry and in biomedical field.[10-12] Doping of transition metal (TM) ions into the host material will give a useful approach to know their structural and optical properties.

Influences of copper ions are more on optical and electrical properties of materials which cause attention to them.[13,14] Copper generally exists in Cu^+, Cu^{2+} states and less frequently as Cu^{3+}, Cu^+ and Cu^{3+} both are diamagnetic and hence Electron Paramagnetic Resonance (EPR) inactive. Cu^{2+} is the most stable paramagnetic ion which is widely used as a probe in many a system.[15] EPR is a unique tool to find the sites available for the impurity and the covalency of metal-ligands bonds. Optical absorption study is supplementary to EPR spectroscopy that gives information on the ordering of energy levels, bonding of different complexes and also site symmetry of the metal ions in a system. The objective of this article is to prepare Cu^{2+} ions doped CZP nanophosphor by solid-state reaction (SSR) method, to investigate the structural information and optical properties. However, by thorough literature survey, no reports have been found about EPR, optical and Fourier transformed infrared (FT-IR) studies of TM ions doped CZP. In the present investigation, X-ray Diffraction (XRD), FT-IR, Optical and EPR studies are used to get details about the crystal structure, vibration bands, local site symmetry and bonding nature of metal ions with ligands.

EXPERIMENTAL

Material and Methods

Calcium carbonate ($CaCO_3$), Zinc oxide (ZnO), Di-Ammonium hydrogen orthophosphate [$(NH_4)_2HPO_4$] and CuO were procured from Sigma-Aldrich Corp. All these chemicals are of first grade and used without any refinement. In order to prepare the sample, 1.0009 g of $CaCO_3$, 1.6274 g of ZnO and 2.6412 g of [$(NH_4)_2HPO_4$] are weighed as per stoichiometric ratios and allowed for 30 min grinding with aid of an agate mortar and pestle. The grinding process is extended for 1 more hour by adding CuO (0.0079 g) to the mixture obtained earlier. Now the final chemical composition was collected into a crucible then heated and annealed at 500 ^oC in the air for 2 hours using muffle furnace to expel NH_3, CO_2 and other impurities. The annealing process is repeated at 1000 ^oC for 2 hours, anticipated by grinding for 30 minutes to obtain a fine powder of copper ions doped $CaZn_2(PO4)_2$.

Characterization Techniques

The XRD pattern of Cu^{2+} ions doped $CaZn_2(PO_4)_2$ nanophosphor was recorded using Shimadzu XRD 6100 diffractometer with Cu Kα radiation (1.5406Å). Fourier transform infrared (FT-IR) spectrum was obtained from Shimadzu IRAffinity 1S FT-IR spectrophotometer in 400-4000 cm^{-1} region. The optical absorption spectrum was recorded on JASCO V670 spectrophotometer in the range 200-1400 nm. JES-FA EPR spectrometer was used for EPR spectrum at room temperature with X-band and 100 KHz field modulations.

RESULTS AND DISCUSSION

Powder X-Ray Diffraction Studies

The structure of the developed nanophosphor was confirmed by analyzing its powder X-ray diffraction pattern. XRD pattern of Cu^{2+} ions doped $CaZn_2(PO_4)_2$ nanophosphor is shown in the Fig.-1 and exhibited good agree well with the standard JCPDS data (84-1578). The XRD pattern indicates triclinic structure with lattice cell parameters are evaluated as a = 0.496 nm, b = 0.8418 nm, c = 0.8940 nm, α = 113.75°, β = 102.45° and γ = 94.20°. The peaks of nanophosphor sample shifted slightly towards the lower scattering angle of 2θ. If TM ion ionic radius is smaller than that of Ca^{2+} ion, the pattern switches over to higher values of 2θ. In contrast to this, the pattern tilts towards lower angles of 2θ if the ionic radius of TM ion is large compared to that of Ca^{2+} ion. After careful examination, the peaks shifted towards lower values of 2θ as copper's ionic radius is greater than that of calcium ion. From the pattern, it is obvious that the diffraction peaks are very sharp without much broadening. Hence the nanophosphor was crystalline in nature. The size of nanophosphor was estimated in accordance with Debye-Scherrer's formula given by $D = 0.9\ \lambda/\beta\cos\theta$, where k is a constant called shape factor and have the value 0.9, λ is the X-rays wavelength (1.5406Å), θ is Bragg's angle for high intense peak, and β is width of the peak at half maximum corresponding the lattice planes. Based on β values of a maximum intense peak, the average grain size is measured as 82.28 nm. The dislocation density (δ) and micro strain (ε) are calculated using the equations $\delta = 1/D^2$ and $\varepsilon = \beta \cos\theta /4$ respectively, which were evaluated as $\delta = 0.1 \times 10^{15}/m^2$ and $\varepsilon = 0.4 \times 10^{-3}$.

FT-IR Studies

Figure-2 shows FTIR spectrum of Cu^{2+} ions doped $CaZn_2(PO_4)_2$ nanophosphor. It exhibits the vibration bands in the range 400-4000 cm^{-1}. The spectrum manifests all the 4 types of vibrational modes of phosphate (PO_4^{3-}) ion. The vibrational band observed at 2352 cm^{-1} is attributed to CO_2 band[16-18]. C=O stretching of carbonyl group occurs at 1735 cm^{-1}. Generally, isolated phosphate (PO_4^{3-}) ions with tetrahedral symmetry are observed in phosphates with four fundamental modes of vibrations[19-21]. They are non-degenerate symmetric stretching (ν_1), doubly degenerate symmetric bending (ν_2) and triply degenerate asymmetric stretching and bending (ν_3 & ν_4) modes of vibrations. Here the four modes occur at 970 (ν_1), 360 (ν_2), 1080 (ν_3) and 550 cm^{-1} (ν_4). In solids, the PO_4^{3-} ion is actually distorted from T_d symmetry. Due to this ν_1 and ν_2 modes are made to appear in the infrared region. The ν_3 mode appears in two components at 1172 and 1075 cm^{-1} [22,23].

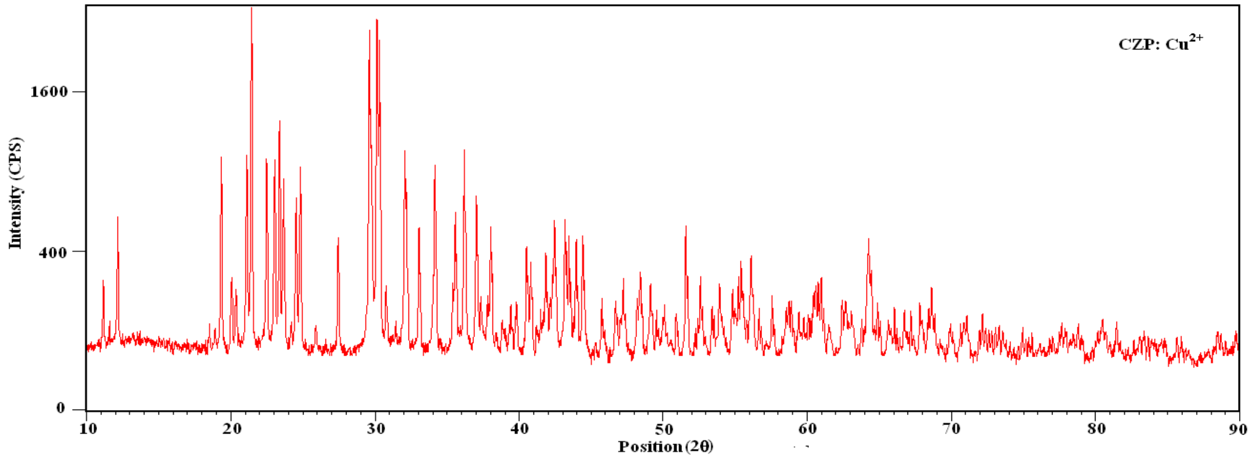

Fig.-1: X-Ray Diffraction Pattern of Cu^{2+} Doped $CaZn_2(PO_4)_2$ Nanophosphor

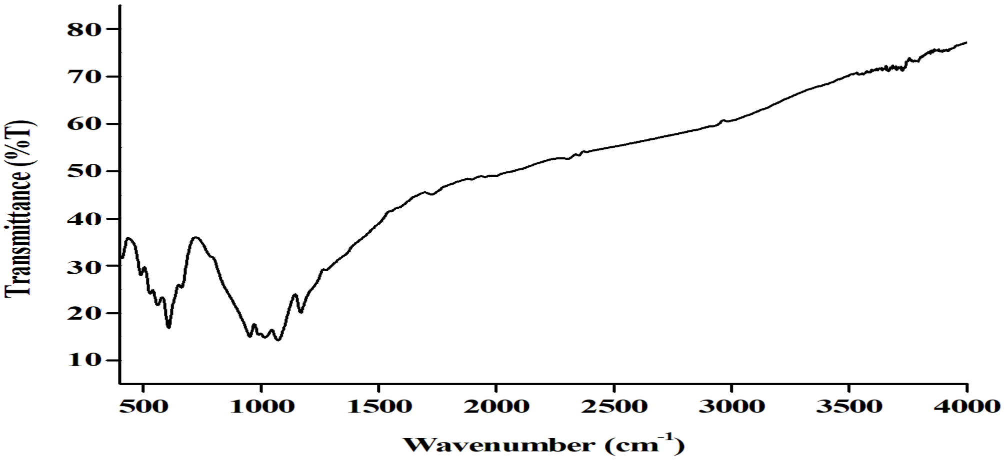

Fig.-2: FT-IR Spectrum of Cu^{2+} Doped $CaZn_2$ $(PO_4)_2$ Nanophosphor

The band at 950 cm^{-1} is assigned to symmetric stretching (ν_1) of phosphate ion[24]. The vibrational bands at 602, 547 and 519 cm^{-1} belong to ν_4 mode [23,24]. 484 cm^{-1} band represents symmetric bending (ν_2) of PO_4^{3-} group[25]. The band at 665 cm^{-1} is imputed to the CH_2 bending mode of vibration [26]. The vibrational bands assigned with corresponding values are listed in Table-1.

UV-VIS Spectral Studies

The optical absorption spectrum of Cu^{2+} ions doped $CaZn_2(PO_4)_2$ nanophosphor can be seen from Fig.-3. $3d^9$ electronic configuration is possessed by divalent copper ion. In octahedral crystal fields, there occurs only one electronic transition $^2E_g \rightarrow {}^2T_{2g}$ for copper ion. The ground state ^2E_g is unstable as copper obeys Jahn-Teller effect and the symmetry may be lowered as tetragonal or rhombic. For Cu^{2+} ion, four d-d transitions are expected for the rhombic field while three transitions are observed in the tetragonal field. A glance at the diagram infers that four bands are noted which indicate that Cu^{2+} ions have deviated from octahedral symmetry. In rhombic symmetry the energy level ordering is $^2A_1(d_{x2-y2}) < {}^2A_1(d_{z2}) < {}^2A_1(d_{xy}) <$

$^2B_1(d_{xz}) < {}^2B_2(d_{yz})$[27]. The observed bands at 689, 830, 1050 and 1207 nm are liable to the transitions $^2A_1(d_{x^2-y^2}) \rightarrow {}^2B_2(d_{yz})$, $^2A_1(d_{x^2-y^2}) \rightarrow {}^2B_1(d_{xz})$, $^2A_1(d_{x^2-y^2}) \rightarrow {}^2A_1(d_{xy})$ and $^2A_1(d_{x^2-y^2}) \rightarrow {}^2A_1(d_{z^2})$ respectively.[28] These bands are characteristic of Cu^{2+} ions distorted rhombically in octahedral co-ordination. There is harmony between these results and copper ions doped other complexes.[29, 30]

Table-1: The Band Head Data and Assignments in FT-IR Spectraum of Cu^{2+} Doped $CaZn_2(PO_4)_2$ Nanophosphor

Vibrational Frequencies (cm^{-1})	Band Assignment
484	Symmetric Bending Mode of PO_4^{3-} (ν_2)
519, 547, 602	Asymmetric Bending Modes of PO_4^{3-} (ν_4)
665	CH_2 Bending
950	Symmetric Stretching of PO_4^{3-} (ν_1)
1172, 1075	Asymmetric Stretching of PO_4^{3-} (ν_3)
1735	C=O Stretching
2352	CO_2

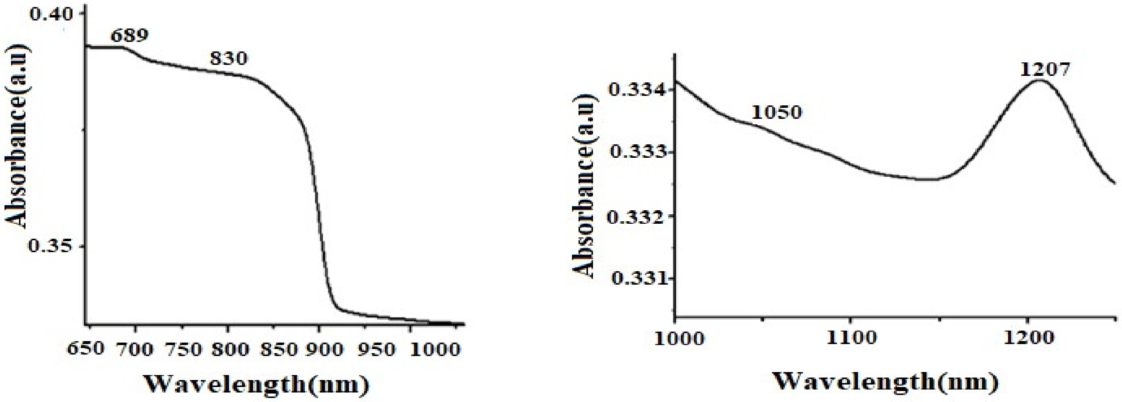

Fig.-3: Optical Absorption Spectrum of Cu^{2+} Doped $CaZn_2(PO_4)_2$ Nanophosphor

EPR Studies

The EPR spectrum of Cu^{2+} ions doped $CaZn_2(PO_4)_2$ nanophosphor at room temperature is depicted in Fig. -4. The spectrum exhibited three resonance signals which lie in the low field (g_1), mid field (g_2) and high field (g_3) regions.

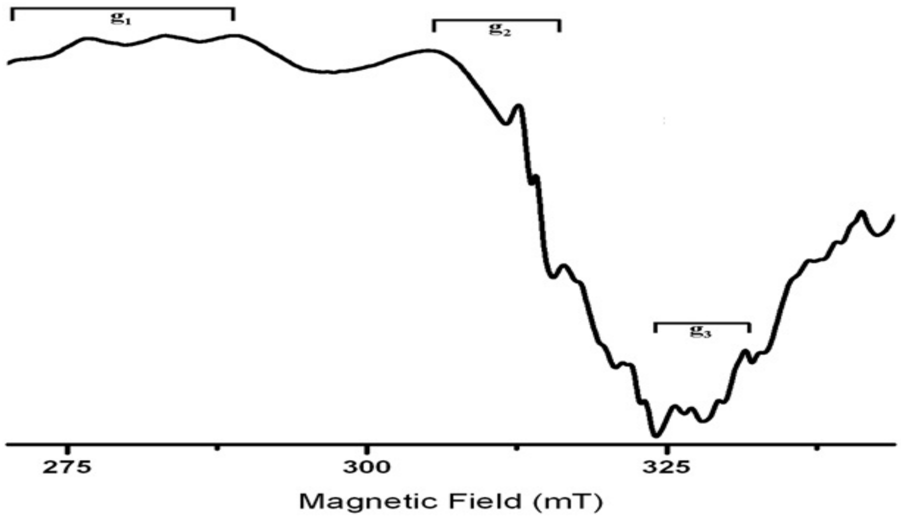

Fig.-4: EPR Spectrum of Cu^{2+} Doped $CaZn_2(PO_4)_2$ Nanophosphor

Each field comprises four lines (Quartet structure) which are transparent from the Fig.-4. The Spin-Hamiltonian parameters (g-factors) and hyperfine splitting constants (A values) were derived from the field strengths at the peak positions. The values come out to be $g_1 = 2.417$, $g_2 = 2.172$, and $g_3 = 2.066$, and $A_1 = 60\times10^{-4}$ cm^{-1}, $A_2 = 37.33\times10^{-4}$ cm^{-1} and $A_3 = 30.33\times10^{-4}$ cm^{-1}. The g-values are in correlation with those reported for Cu^{2+} ions doped complexes[27-29]. The observed quartet structures in the EPR spectrum confirm the rhombically distorted nature of Cu^{2+} ions in the CZP lattice. The information about the ground state (G.S) of Cu^{2+} ions can easily be deduced from the above data. If $g_1 > g_2 > g_3$ and $R=(g_2-g_3)/(g_1-g_2) >1$ then the ground state term for Cu^{2+} ions is $^2A_1(d_{z^2})$ otherwise for lower R values ($R<1$), the ground state term will be $^2A_1(d_{x^2-y^2})$[31]. In this case, the present evaluated value of R is less than unity which is 0.43 and confirmed the ground state. With the help of Kivelson and Neiman formula[27] and presuming P as 0.36 cm^{-1}, $g_e = 2.0023$, the Covalency parameter (α^2) is assessed from the formula given by-

$$\alpha^2 = 7/6\{(A_3-A_1)/P-(g_e-g_1) + 11(g_e-g_3)/14-6(g_e-g_2)/14\}$$

The magnitude of α^2 turns out as 0.0189 which implies that $\alpha = 0.137$. This value strongly supports the covalent nature.

CONCLUSION

In summary, copper ions doped $CaZn_2(PO_4)_2$ nanophosphor was successfully prepared by solid-state reaction method. XRD studies reveal that the structure belongs to triclinic crystal. The average crystallite size is calculated as 82 nm which confirmed the order of nanoscale. FT-IR spectrum exhibited different characteristic vibration bands of phosphate (PO_4^{3-}) ion. Optical and EPR spectrum evidences the rhombically distortion from the regular octahedral co-ordination for Cu^{2+} ions. The bonding parameter (α) is the sign of covalent bonding between Cu^{2+} ions and its ligands.

ACKNOWLEDGMENT

Authors are thankful to UGC-DSA1 (F.530/11/DSA-I/2015 (SAP-I) and DST-FIST (F.No. SR/FST/PSI-163/2011(C)) New Delhi for providing financial assistance to the Dept. of Physics, Acharya Nagarjuna University to carry out present research work. Authors would like to thank the Head, SAIF, IIT Madras for providing EPR recordings.

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[RJC-5261/2019]