

Synthesis XRD TEM and Optical Absorption Spectroscopic Characterization of Copper Doped Nano Apatite

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Abstract- Synthesized copper doped chloro-apatite has been characterized by XRD, TEM, Optical and NIR spectroscopy. XRD pattern indicates that the compound shows hexagonal structure with lattice constants of $a = b = 9.027 \text{ \AA}$ and $c = 13.767 \text{ \AA}$. TEM images suggest that nano crystals are closely joined together and form agglomerates with rod in shape and are parallel. The optical spectrum exhibits a number of electronic bands due to presence of Cu(II) ions in the compound. The bands in NIR spectra are due to the overtones and combinations of water and phosphate molecules.

Keywords- Copper Doped Chloro-Apatite; XRD; TEM; Optical Absorption; NIR Spectroscopy

I. INTRODUCTION

Apatites are phosphate containing minerals with the general formula $\text{Ca}_5(\text{PO}_4)_3\text{X}$, where $\text{X} = \text{Cl, F, OH}$. This group of minerals is classified as follows [1]:

Fluoro-apatite	$\text{Ca}_5[\text{PO}_4]_3\text{F}$
Chloro-apatite	$\text{Ca}_5[\text{PO}_4]_3\text{Cl}$
Hydroxyapatite	$\text{Ca}_5[\text{PO}_4]_3\text{OH}$
Carbonate-apatite	$\text{Ca}_3[\text{PO}_4, \text{CO}_3, \text{OH}]_3(\text{F, OH})$.

Of these minerals fluoro-apatite is the most common and stable mineral. Apatite is the most suitable ceramic material for hard tissue. It is the main constituent of teeth and bones [2]. Also, it has wide application in the manufacture of fertilisers, phosphoric acid, fluorescent light materials and detergents. The crystal structure of natural apatite is reported as hexagonal system with space group $\text{P6}_3/\text{m}$ having cell dimensions $a = b = 9.37 \text{ \AA}$, $c = 6.88 \text{ \AA}$ and $Z = 2$. Each chloride ion is surrounded by three Ca atoms at one level and in addition $-\text{CaO}$ columns are linked with the PO_4 group forming a hexagon [3]. The compact arrangement of PO_4 groups in the structure provides two kinds of channels containing Ca ions. The unit cell contains i) four Ca(II) ions in column parallel to the c-axis and surrounded by nine oxygens and ii) six Ca(II) ions are surrounded by six oxygens and one OH [4]. The incorporation of foreign cations in the apatite lattice is expected to change the bulk properties. The structures of a number of synthetic substituted apatites are investigated to evaluate the structural changes associated with the substitution [5]. The influence of transition metal ions in the host lattice plays an important role in the understanding of the structural variations. In the present work, the preparation and the spectral properties of nano crystals of Cu doped chloro-apatite is studied using XRD, TEM and Optical absorption spectroscopy.

II. THEORY

The electronic configuration of Cu(II) is $[\text{Ar}] 3d^9$. In an octahedral crystal field, the corresponding ground state electronic configuration is $t_{2g}^6 e_g^3$ which yields 2E_g term. The excited electronic configuration, $t_{2g}^5 e_g^4$ corresponds to ${}^2T_{2g}$ term. Thus only one single electron transition ${}^2E_g \rightarrow {}^2T_{2g}$ is expected in an octahedral crystal field. Normally, the ground 2E_g state is split due to Jahn-Teller effect and hence lowering of symmetry is expected for Cu(II) ion and this state splits into ${}^2B_{1g}(d_x^2 - y^2)$ and ${}^2A_{1g}(d_z^2)$ states in tetragonal symmetry and the excited term ${}^2T_{2g}$ also splits into ${}^2B_{2g}(d_{xy})$ and ${}^2E_g(d_{xz}, d_{yz})$ levels. In rhombic field, 2E_g ground state splits into ${}^2A_{1g}(d_x^2 - y^2)$ and ${}^2A_{2g}(d_z^2)$ whereas ${}^2T_{2g}$ splits into ${}^2B_{1g}(d_{xy})$, ${}^2B_{2g}(d_{xz})$ and ${}^2B_{3g}(d_{yz})$ states. Thus, three bands are expected for tetragonal (C_{4v}) symmetry and four bands are expected for rhombic (D_{2h}) symmetry [6]. The wave numbers of the three different transitions are given by the following equations in the tetragonal field are [7] given in Fig. 1.

$${}^2B_{1g} \rightarrow {}^2A_{1g}: 4Ds + 5Dt$$

$${}^2B_{1g} \rightarrow {}^2B_{2g}: 10Dq$$

$${}^2B_{1g} \rightarrow {}^2E_g: 10Dq + 3Ds + 5Dt$$

In the above formulae Dq is crystal field and Ds , Dt are tetragonal field parameters.

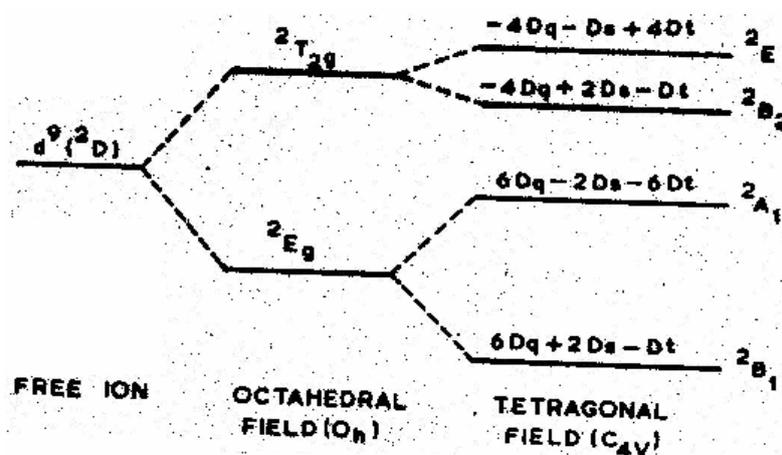


Fig.1 Energy level diagram of Jahn-Teller distortion in d-orbital in octahedral tetragonal field

III. EXPERIMENTAL

A. Synthesis of Copper Doped Apatite Nano Crystals

All reagents used for the synthesis of copper doped apatite nano crystals were of analytical grade. Double distilled water was used for the preparation of the required solution. 10 g of calcium chloride, 6 mL of phosphoric acid and 0.1 g of cupric acetate were mixed in agate mortar. All the above chemicals were grounded finely and added 100 mL water. The mixture solution was taken in a reflux flask of 250 mL with magnetic stirrer and kept in cavity of CATA-2R microwave reactor which was supplied by Catalyst Systems, Pune, India. The reaction was performed at 60 °C for 5 minutes in the reactor. The solution becomes turbid by the formation of copper doped chloro-apatite abbreviated as CCAP nano crystals. The solution was allowed to cool to room temperature and then filtered using a suction pump. The product was collected by filtration, washed with water and dried by keeping in a dessicator for about three days. The product was copper doped chloro-apatite.

B. Spectral Techniques

The X-ray powder diffraction pattern of the Cu doped chloro-apatite sample was recorded in reflection geometry on a Philips X-ray diffractometer operating at 30 mA, 40 kV with a Cu-K α ($\lambda = 1.54060 \text{ \AA}$) source at 25°C from 10°–75°. Data were collected using a continuous scan rate of which was then refined into 2θ of 0.02° per step. The TEM images were obtained on a Philips CM 200 transmission electron microscope operating at 200 kV with a resolution of 0.23 nm. An optical absorption spectrum of the Cu doped chloro-apatite sample in a mull form was recorded at room temperature on a Carey 5E UV-Vis-NIR spectrophotometer with wavelengths ranging from 200–2500 nm. Band component analysis was performed using the Jandel "PEAKFIT" software package (Lakshmi reddy et al., 2006), which enabled the type of fitting functions to be selected and specific parameters to be fixed or varied accordingly. Band fitting was conducted using a Lorentz–Gauss cross product function with a minimum number of component bands during the fitting process. The Lorentz–Gauss ratio was maintained at values greater than 0.7, and fitting was performed until reproducible results were obtained with squared correlations of r^2 greater than 0.9975.

IV. RESULTS AND DISCUSSION

A. X-ray Diffraction Results

Fig.2 presents the X-ray diffraction pattern of copper doped apatite nano compound recorded on Philips diffractometer at 25 °C. The peaks were characterized by using Scherrer formula. The X-ray peak list of synthesized copper doped apatite nano-crystal is shown in Fig.2. The unit cell constants are $a = b = 9.027 \text{ \AA}$, $c = 13.767 \text{ \AA}$. XRD results confirm that the product was a pure hexagonal phase of $(Ca,Cu)_5(PO_4)_3Cl$. The decrease in cell constants when compared to bulk sample indicates that there

may be some surface tension in the nano-crystals. The crystallite size of the compound was evaluated from the line broadening of the peaks using Debye Scherrer equation $D_{(hkl)} = \frac{0.9\lambda}{\beta_{1/2} \cos\theta}$

Where D is the average crystallite size of the crystal, θ is the corresponding Bragg angle, λ is the wavelength of incident X ray, $\beta_{1/2}$ is the full width at half the maximum (FWHM) height of the peak. The crystallite size of the crystal, 100 nm, is calculated from the XRD pattern.

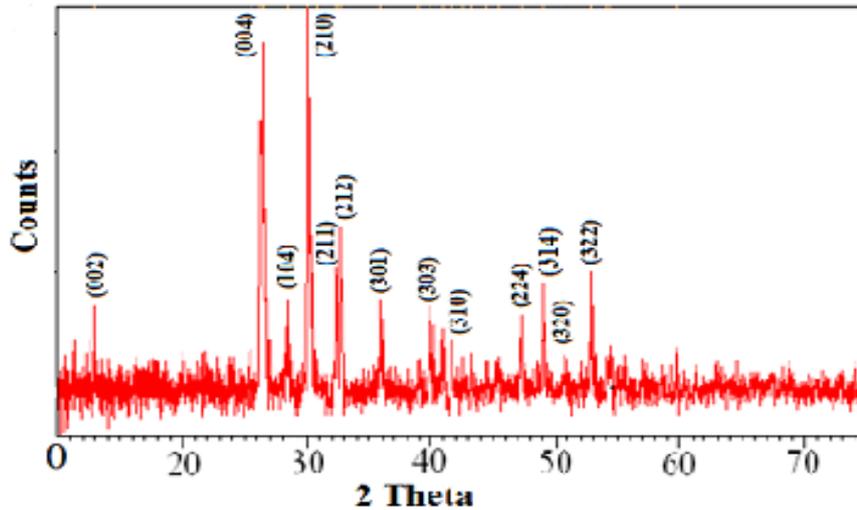


Fig.2 XRD pattern of synthetic Cu doped chloro apatite nano crystal

B. Transmission Electron Microscope

Fig. 3 shows the typical bright field TEM images of the synthesized copper doped chloro apatite (CCAP) nano-particles. It is observed from the image that the crystal structure is hexagonal and the particles are rod in shape and are parallel. These are joined together to form agglomerates. The particles are having size of 130.08, 170.57, 373.49, 156.68, 437.94 and 482.87 nm. Thus the mean dimensions of the copper doped chloro-apatite nano-rods are 130 nm to 483 nm.

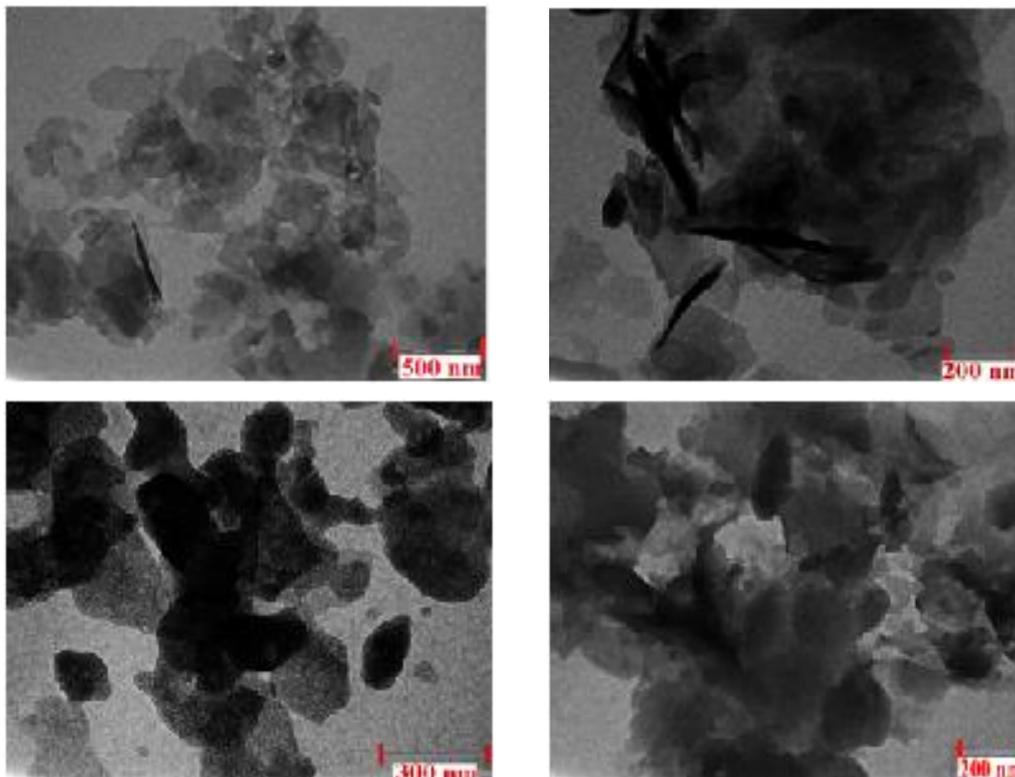


Fig. 3 TEM micrographs of copper doped chloro-apatite nano particle

C. Optical Absorption Spectral Studies

The total optical absorption spectrum of CCAP nano-crystals that was recorded in the mull form at room temperature from 200–2500 nm is shown in Fig. 4.

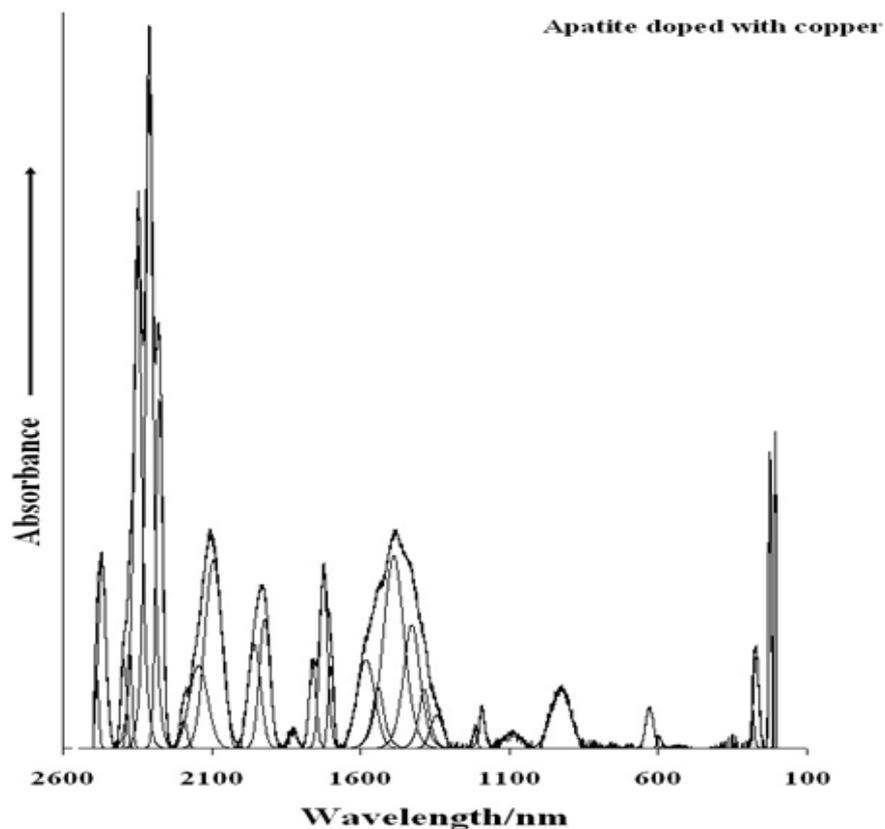


Fig.4 Total optical absorption spectrum of Cu doped chloro-apatite nano crystals from 200 to 2500 nm at room temperature, shown separately in five successive wavelength ranges.

The band component analysis was conveniently divided into several ranges, as shown in Figs. 4(a)–(e).

1) *The 50000 (200 nm) to 7700 (1300 nm) cm⁻¹ Spectral Region:*

Fig. 4(a) & (b) presents the band component analysis spectrum in the range of 200- 1300 nm. consisting of bands at 8230, 8400, 10750, 15870, 16805, 35715, 37035, 44440 and 48780 cm⁻¹ in the UV –Vis and NIR regions.

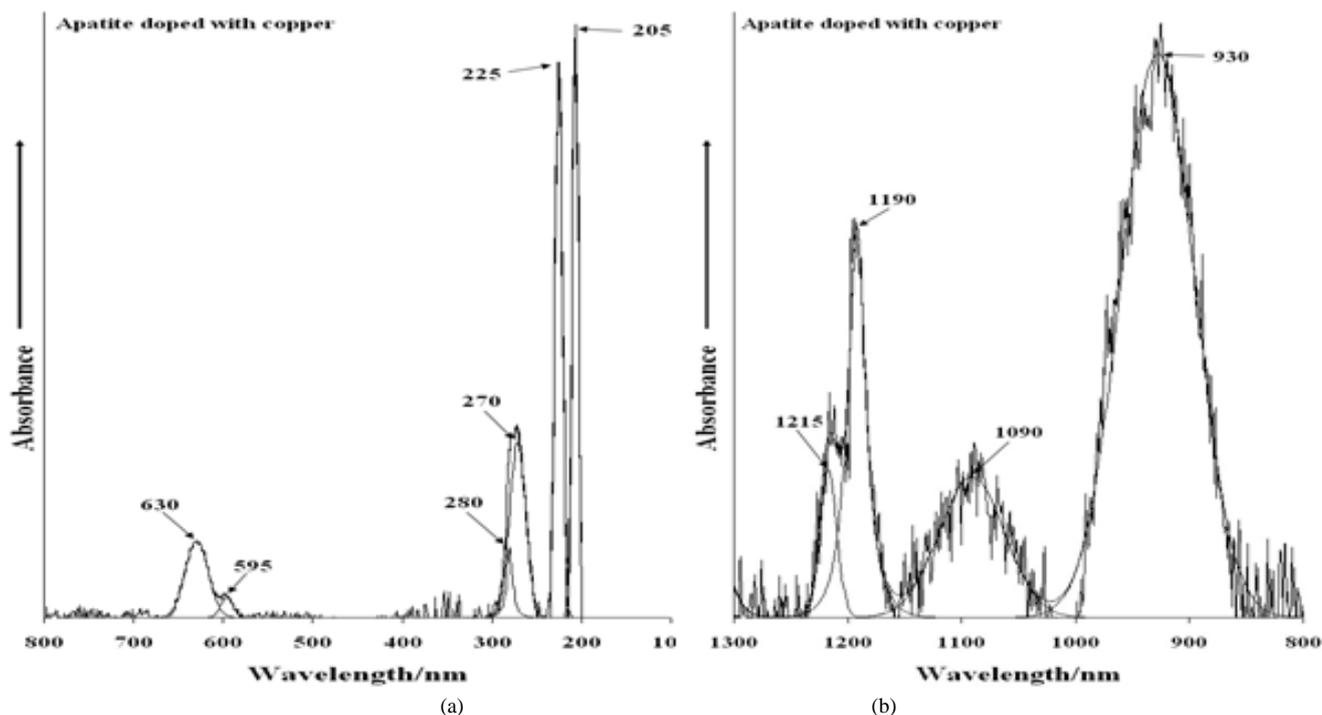


Fig. 4(a) & (b) The band component analysis spectrum in the range of 200- 1300 nm

The bands observed at 35715, 37035, 44440 and 48780 cm^{-1} are charge transfer transition. For easy analysis of the spectrum, the bands are divided into two sets: 8400, 10750 and 15870 cm^{-1} as first set and 8400, 10750 and 16805 cm^{-1} as second set. The two sets of bands are attributed to Cu(II) ion. These bands are attributed for the transitions from ${}^2B_{1g}$ to 2E_g (8400 cm^{-1}), ${}^2B_{2g}$ (10750 cm^{-1}) and ${}^2A_{1g}$ (15870 and 16805 cm^{-1}) respectively. Based on these assignments and using the equations given in theory the octahedral field (Dq) and tetragonal field (Dt and Ds) parameters are evaluated to be Dq= 1075 cm^{-1} , Ds = 1931, 2065 cm^{-1} and Dt = 135,28 cm^{-1} . The same sign of Dq and Dt indicates axial elongation [8-9]. The results indicate that copper is not entered in equal proportions of two different sites of Ca(II) ions site of apatite. Further it could be presumed that larger Dt value indicates that strong preference is there for Ca the first site and lesser value for Ca the second site.

The band observed at 8230 cm^{-1} (3220 + 1620 + 3400 = 8240 cm^{-1}) is attributed to ($\nu_1 + \nu_2 + \nu_3$) combination of water [10].

2) The 7700 (1300 nm) to 5500 (1800 nm) cm^{-1} Spectral Region:

Water has three fundamental modes. They are symmetric OH stretch (ν_1), H-O-H bending mode (ν_2) and asymmetric OH stretch (ν_3). In solid they will appear at 3220 (ν_3), 1620 (ν_2) and 3400 (ν_1) cm^{-1} [11]. The shifting of ν_1 and ν_3 towards lower frequency side and ν_2 towards higher frequency is due to hydrogen bonding [10]. The fundamental vibration modes of phosphate are $\nu_1 = 980$, $\nu_2 = 363$, $\nu_3 = 1083$ and $\nu_4 = 515$ cm^{-1} [12]. In the copper phosphate minerals phosphate vibrations centre occur in the range 990-950 cm^{-1} as symmetric stretch (ν_1), 480-400 cm^{-1} symmetric bending (ν_2) region, 1090-1030 cm^{-1} anti-symmetric stretching region (ν_3) and 650-500 cm^{-1} out-of-plane bending modes (ν_4) [13]. The overtone and combination frequencies are expected in the near infrared region [14].

Fig. 4(c) shows near infrared spectrum of copper doped apatite nano-crystals in 7700 – 5500 cm^{-1} region. In this region very one sharp and another sharp and broad band with several component bands are observed. The assignments of these bands are as follows. The three component bands observed at 7435, 7220 and 6990 cm^{-1} are attributed to combinations of water fundamentals. The very sharp band observed at 6710 cm^{-1} is due to ($2\nu_2 + \nu_3$) combination of H_2O . Also the band observed at 6490 cm^{-1} is identified as combination of ($\nu_1 + 2\nu_2$) water. The two prominent features involve the fundamental stretching combined with the fundamental Cu-O-H bend to give the band at 4770 cm^{-1} with first overtone of the band at 5880 cm^{-1} . Accordingly the first sharp band observed at 5795 cm^{-1} with shoulders on either side at 5680 and 5880 cm^{-1} is assigned to Cu-O-H bend.

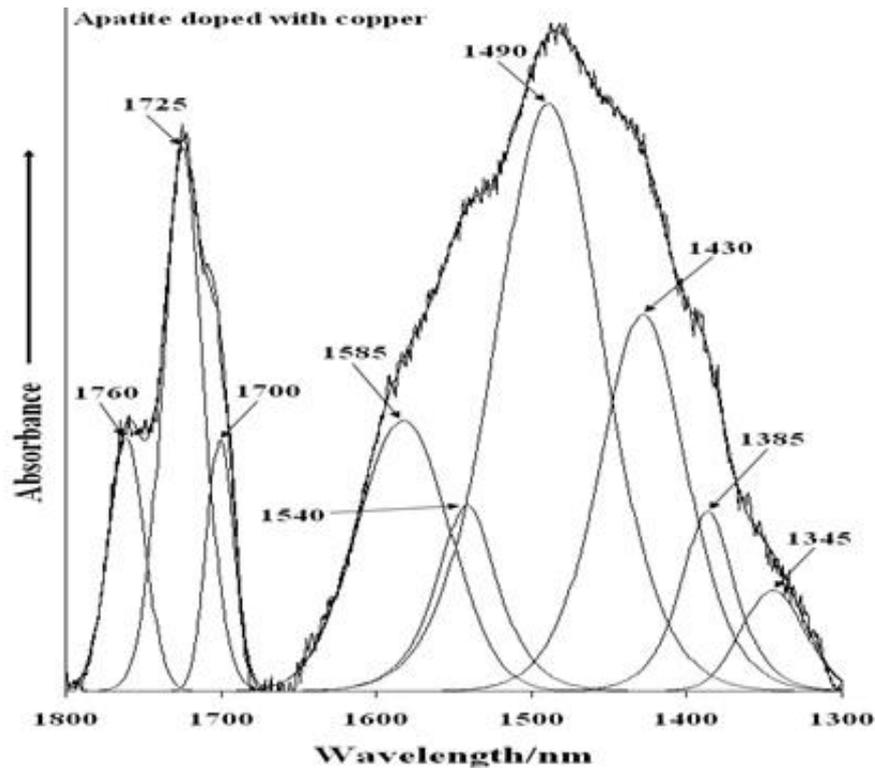


Fig. 4 (c) Near infrared spectrum of copper doped apatite nano-crystals in $7700 - 5500 \text{ cm}^{-1}$ region

3) The $4400 (2250 \text{ nm})$ to $5500 (1800 \text{ nm}) \text{ cm}^{-1}$ Spectral Region:

The MIR spectrum of compound is shown in Fig. 4(d). The prominent sharp band observed at 4770 cm^{-1} with components at $4660, 4555 \text{ cm}^{-1}$ is assigned to fundamental stretching combined with the fundamental Cu-O-H bend. The average of two bands observed at 5205 and 5115 cm^{-1} is 5160 cm^{-1} is the combination band at 4770 cm^{-1} [15].

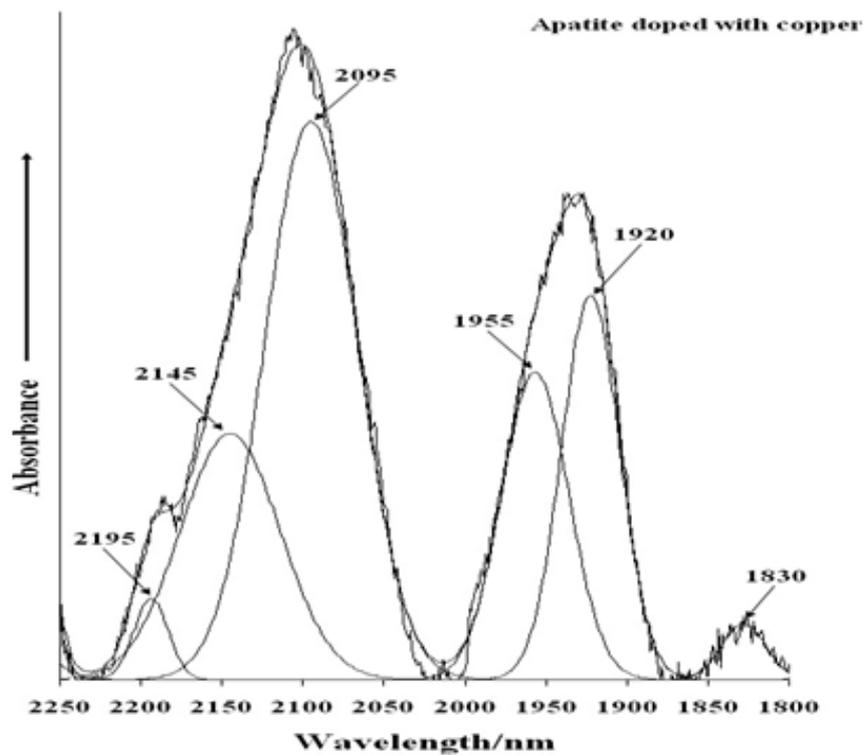


Fig. 4(d) The MIR spectrum of compound

4) The $4400 (2250 \text{ nm})$ to $4000 (2500 \text{ nm}) \text{ cm}^{-1}$ Spectral Region:

Fig. 4(e) shows MIR spectrum of compound in the range 4400- 4000 cm^{-1} . In Fig. 4(e), it shows two weak bands at 4210 and 4175 cm^{-1} . Sharp profile of bands centered at 4330 cm^{-1} with component shoulders on either side at 4395 and 4255 cm^{-1} do not belong to the metal ion. Therefore these bands are assigned to vibrational frequencies of phosphate radical. These values presented in Table 1 are in good agreement with those of the observed values.

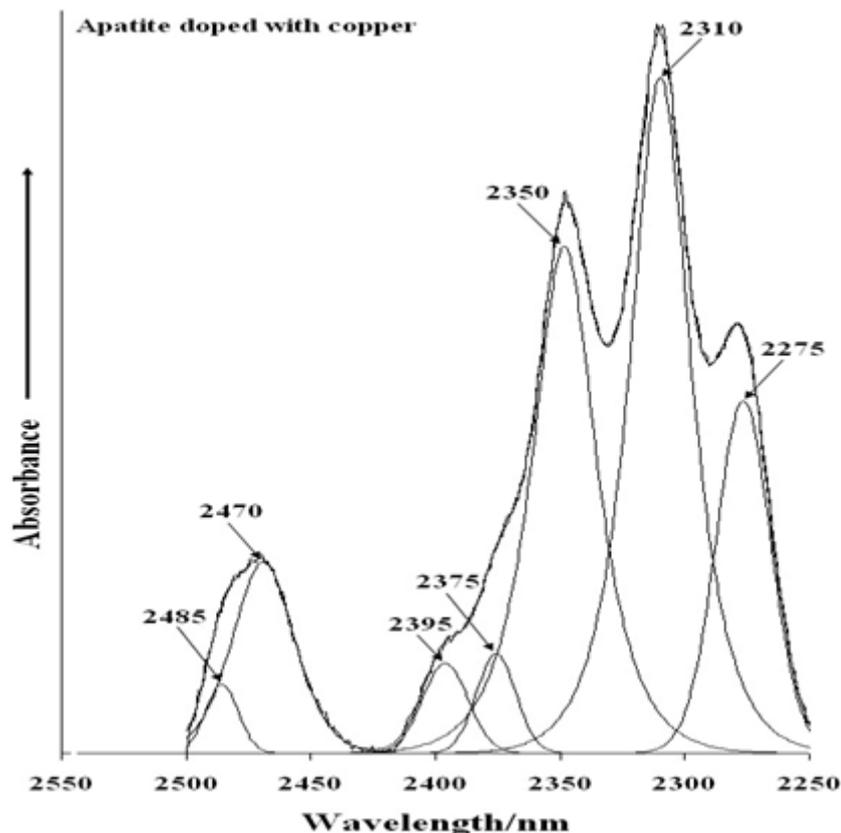


Fig. 4(e) MIR spectrum of compound in the range 4400- 4000 cm^{-1}

TABLE I BAND HEAD ASSIGNMENTS FOR PHOSPHATE ION IN Cu DOPED CHLORO-APATITE NANO COMPOUND

Observed		Assignments	Calculated cm^{-1}
nm	cm^{-1}		
2470	4050	$2\nu_1 + 3\nu_3 + 2\nu_4$	4079
2395	4175	$\nu_1 + 2\nu_3 + 2\nu_4$	4176
2350	4260	$3\nu_3 + 2\nu_4$	4279
2310	4330	$3\nu_1 + \nu_2 + 3\nu_4$	4333
2275	4395	$3\nu_1 + \nu_2 + \nu_3$	4386

V. CONCLUSIONS

- 1) The synthesized Cu doped nano chloro-apatite was highly crystalline.
- 2) XRD results indicated that the apatite had pure hexagonal phase with lattice constants $a = b = 9.027 \text{ \AA}$, $c = 13.767 \text{ \AA}$.
- 3) TEM images revealed that the particles were cylindrical in shape and agglomerating in the structure. The crystal structure was hexagonal.
- 4) XRD and TEM analyses confirmed the nanocrystalline nature of the synthesized Cu doped chloro-apatite.
- 5) Optical absorption spectrum was characterized by the Cu^{2+} in the Cu doped chloro-apatite, indicating that Cu(II) is in a tetragonal elongated distorted octahedral structure. Also copper is not entered in Ca two sites in equal proportions of the structure of the compound.
- 6) NIR results were due to the fundamental vibrations of water and phosphate molecules which were supporting the formula of the compound.

REFERENCES

- [1] W. A. Deer, H. A. Howie, J. Zussman. *An Introduction to the Rock Forming Minerals*, ELBS, London, 1976.

- [2] W. Suchanek and M. Yoshimura. Processing and properties of hydroxyapatite-based biomaterials for use as hard tissue replacement implants, *Journal of Material Research*, vol. 13, pp. 94-117, 1998.
- [3] W. L. Bragg, *Atomic Structure of Minerals*, Cornell University Press, 1937.
- [4] Park Hwan-Soo, Kim In-Tae, Kim Hwan-Young, Lee Kyu-Seong, Ryu Seung-Kou and Kim Joon-Hyung. Application of apatite waste form for the treatment of water-soluble wastes containing the Radioactive elements Part I: Investigation of the possibility, *J. Ind. Eng. Chem. Modern Geology*, vol. 8, pp. 318-327, 2002.
- [5] Mathew Mathai and Takagi Shozo, Structure of Biological Minerals in Dental research, *Journal of Resonance, Natural, Institute Standard Technology*, vol. 106, pp. 1035-1044, 2001.
- [6] M. A. Hitachmann, and T. D., Waite, Electronic spectrum of the hexaaquocopper(2+)ion, *Inorganic chemistry*, vol. 15, pp. 2150-2154, 1976.
- [7] G. D. Jones, Jahn-Teller splittings in the optical absorption spectra of divalent iron compounds, *Physics Review*, vol. 155, pp. 259-261, 1967.
- [8] J. Ferguson, T. E. Wood, and H. J. Guggenheim, Electronic absorption spectra of tetragonal and pseudotetragonal cobalt(II). I. Dipotassium tetrafluorocobaltate, dirubidium tetrafluorocobaltate, dipotassium magnesium tetrafluorocobaltate and dirubidium magnesium tetrafluorocobaltate, *Inorganic Chemistry*, vol. 14, pp. 177-183, 1975.
- [9] B. J. Hathaway and D. E. Billing, The electronic properties and stereochemistry of mono-nuclear complexes of the copper(II) ion, *Coordination Chemistry Reviews*, vol. 5, pp. 143-207, 1970.
- [10] G. R. Hunt, J. W. Salisbury, Visible and near-infrared spectra of minerals and rocks: I, Silicate minerals, *Modern Geology*, vol. 283-300, 1970.
- [11] K. Nakamoto, (1970). *Infrared Spectra of Inorganic and Coordination compounds*, Wiley, New York, 1970.
- [12] G. Herzberg, *Molecular Spectra and Molecular Structures Volume II*, D. Van Nostrand Co., INC, New York, USA. 1966.
- [13] R. L. Frost, T. Klopogge, P. A. Williams, W. Martens, T. E. Johnson and P. Leverett. Vibrational spectroscopy of the basic copper phosphate minerals: Pseudomalachite, ludjibaite and reichenbachite, *Spec. Acta A*, vol. 58, 2861-2868, 2002.
- [14] G. R. Hunt, J. W. Salisbury and C. Lenhoff, Visible and near-infrared spectra of minerals and rocks: V, Halides. Phosphates, arsenates, vanadates and borates *Modern Geology*, vol. 3, pp. 121-132, 1972.
- [15] G. R. Hunt, J. W. Salisbury, Visible and near-infrared spectra of minerals and rocks: IV, Sulphides and sulphates, *Modern Geology*, vol. 3, pp. 1-14 1971.