

Simple and effective way to prepare CuFe₂O₄/SiO₂ nanocomposites by Sol-Gel method

I. Prakash*, P. Muralidharan*, N. Nallamuthu*, M. Venkteswarlu**, N. Satyanarayana*

* Department of Physics, Pondicherry University, Pondicherry- 605 014, India

Corresponding author: E-mail: nallanis2000@yahoo.com

** Present address: Department of Chemical Engineering, NTUST, Taipei, Taiwan

ABSTRACT

Nano-composite containing CuFe₂O₄ nano size crystals embedded in amorphous silica matrix was prepared by Sol-Gel method. The gel of composition 5%CuO-6%Fe₂O₃-89%SiO₂ was synthesized at ambient temperature and heat treated at different temperatures (303 K - 1073 K). X-ray diffraction (XRD), Fourier transform infrared (FTIR), Transmission electron microscopy (TEM) and Differential scanning calorimetry (DSC) were used to characterize the formation of nanocrystals during heat treatment. CuFe₂O₄ nanocrystals were formed from the heat treated gel around 1073 K. The particle size of uniformly distributed CuFe₂O₄ nanocrystals is estimated from TEM micrograph and is found to be 10 to 20 nm in diameter.

Keywords: Sol-Gel, CuFe₂O₄/SiO₂ Nano-composite, DSC, XRD, FTIR and TEM

1 Introduction

Copper ferrites with spinel structure are widely used in magneto-optic recording devices, colour imaging, bio processing, electrical switching, high frequency communication, magnetic refrigeration, etc. devices [1-3]. Recently, due to an advancement of technology, modern scientific world invites materials with better control over their properties, which can be achieved by hybridization of different phases. Composite material is one of those kinds and it combines among crystalline, amorphous and polymer phases to enrich and enhance the properties [4]. Nanomaterials show drastic change in physical and chemical properties over their respective bulk materials due to their quantum confinement [5-8]. Also, the control over the

size and the polydispersity of the nanoparticles is important, since these can change the properties of nanomaterials drastically. Strong supporting matrices like glasses, ceramics and polymers are used to stabilize the nanocrystals, where, nanoparticles are embedded in the supporting matrix to form the nanocomposite structure. Thus, more efforts have been made to develop synthesis methods to prepare nanocrystalline and nanocomposite materials in various forms [9-13]. Sol-gel route has been used effectively to prepare nanocomposites, where, precursors can be mixed in solution form. Therefore, the reaction will be in ionic level and at low temperatures, which can provide good control over the Stoichiometric, homogeneity, structure, purity, etc. of the materials [14]. Hence, the present paper deals with the synthesis, by sol - gel route, and characterization, by XRD, FTIR, DSC and TEM, of uniformly distributed CuFe₂O₄ nanocrystals of 10 to 20 nm size in SiO₂ glassy matrix, forms nano-composite material.

2 Experimental

2.1 Sol – Gel synthesis

Xerogels of Copperferrosilicate were prepared by sol – gel process using precursors of analar grade tetraethylorthosilicate TEOS (Si (OC₂H₅)₄ (Acros organics), Ferric nitrate (s.d. fine-chem), Cupric nitrate (s.d. fine-chem) and ethanol. All precursors were mixed according to the composition 5% CuO – 6% Fe₂O₃ – 89% SiO₂, based on their molecular weight percentage. Fig. 1 shows the flow chart representation of various stages of Sol-Gel process involved in synthesis of CuFe₂O₄/SiO₂ nanocomposite. In fig.1, solution A contains TEOS, ethanol and water. The TEOS and

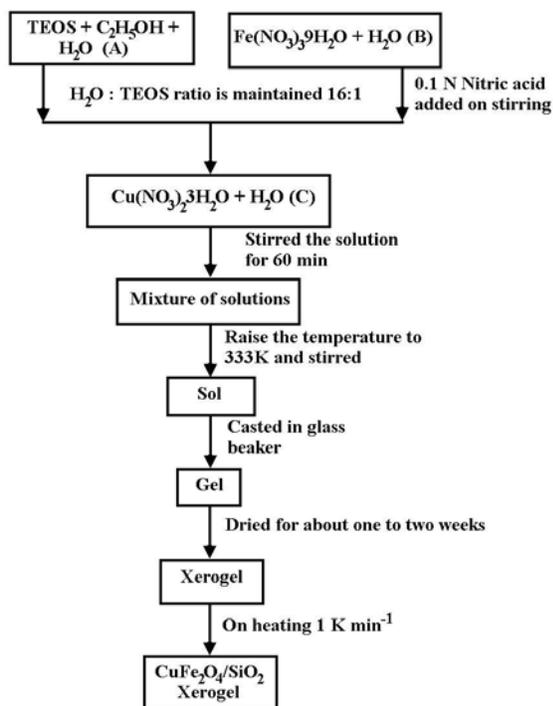


Fig.1. Flow chart for $\text{CuFe}_2\text{O}_4/\text{SiO}_2$ nanocomposite sample preparation by sol-gel process

water ratio was maintained at 1:16 and 2.5 N nitric acid was added as catalyst. An equal volume ratio of ethanol as solvent was mixed with TEOS and water, which was stirred for an hour to get clear transparent solution. Solution B contains required amount of ferric nitrate dissolved in distilled water. Solution B was mixed with solution A and stirred for an hour. Solution C contains required amount of cupric nitrate dissolved in distilled water and was added to A and B solution stirred for two hours at 333 K. The final solution was poured in to a glass beaker covered with aluminum foil and allowed to form gel at ambient temperature. After gelation, holes were punched on the aluminium foil to allow ethanol and water evaporation, formed during condensation. The dried gel was heat treated at various temperatures at the rate of 1 K per minute and it is characterized by XRD, FTIR DSC and TEM to observe the formation of nanocrystals in amorphous SiO_2 matrix.

2.2: XRD, FTIR, DSC and TEM measurements

XRD patterns were recorded for the fine powdered dried gels, using Rigaku miniflex diffractometer with $\text{Cu K}\alpha$ and $\lambda=1.4158 \text{ \AA}$, as source wavelength. Dried gel sample and KBr powder were mixed in 1:20 ratio and grounded into fine powder. Using KBr press, thin transparent pellet samples, prepared at room temperature and higher temperatures, were made and were dried to reduce the moisture content. FTIR spectra were recorded on pellet samples using Shimadzu FTIR/8300/8700 spectrophotometer in the frequency range of $4000 - 400 \text{ cm}^{-1}$ with 2 cm^{-1} resolution for 20 scans. The fine powdered dried gel sample of 3 mg was placed in the aluminum pan with lid and pressed to form a micro pellet. Pellet sample was heated at the rate of 10 K per minute from 303 K to 773 K under nitrogen atmosphere and recorded DSC curves using Mettler Toledo star (e) system module;821e/500/575/414183/528.

3 Results and discussions

Fig.2 shows the XRD patterns of the dried gel powders heat treated at 333 K, 473 K, 673 K and 1073 K. From fig.1, the dried gel powder heated up to 873 K showed broad peak centered at 22° is attributed to the characteristic diffraction of the amorphous phase of SiO_2 . Around 1073 K, new crystalline peaks are observed at 36, 30, 43, 57 and 63 over the broad peak.

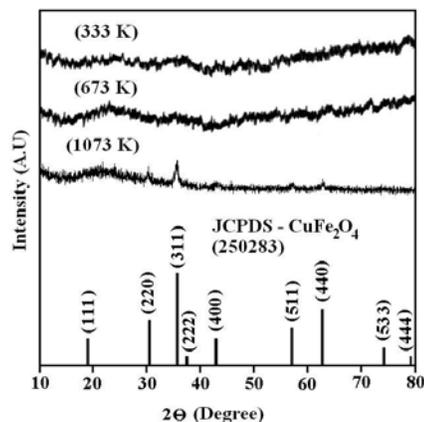


Fig.2. XRD spectra for $\text{CuFe}_2\text{O}_4/\text{SiO}_2$ nanocomposite sample heat treated at various temperatures

The observed 2θ values of the peaks were compared with JCPDS data and confirmed the formation crystalline phase of CuFe_2O_4 cubic structure. The amorphous phase of SiO_2 retained till the sample heated up to 1073 K. Thus, the formation of CuFe_2O_4 crystals in the SiO_2 amorphous matrix forms a composite phase, having both crystalline and amorphous phases in a single material.

Fig. 3 shows the FTIR spectra of the dried gel powders heat treated at 333 K, 673 K and 1073 K and exhibit bands at 3424, 1634, 1383, 1080, 964, 795 and 453 cm^{-1} . The IR bands observed at 3424 and 1634 cm^{-1} are respectively attributed to the OH stretching of water molecules and isolated silanol stretching. The band at 453 cm^{-1} corresponds to the deformation mode of Si-O-Si. The peak at 1383 cm^{-1} is due to the presence of nitrate groups in the sample. The FTIR spectra for higher temperature show the decrease of intensity for the bands at 3424 cm^{-1} , 1634 cm^{-1} and 1383 cm^{-1} , which are due to the removal of water molecules and nitrate groups from the sample [15]. At 1073 K, all the above observed peaks were removed and two new peaks were observed, which indicate that all the impurities like nitrate and other organic groups were completely decomposed from the sample. The observed two new peaks 603 cm^{-1} and 467 cm^{-1} were attributed to the Fe_2O_3 & CuO vibrational modes, indicates the formation of CuFe_2O_4 structure.

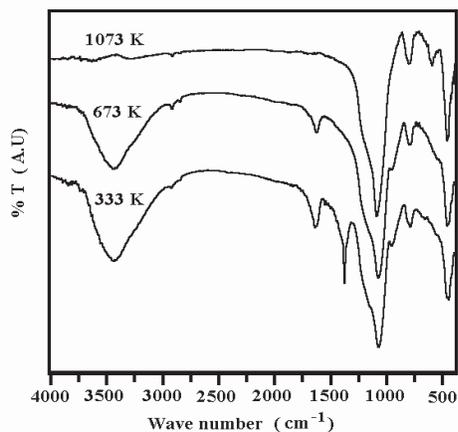


Fig.3. FTIR spectra for $\text{CuFe}_2\text{O}_4 / \text{SiO}_2$ nanocomposite sample heat treated at various temperatures

Hence, the XRD and FTIR results confirm the formation of CuFe_2O_4 crystals in the SiO_2 amorphous matrix and forms a $\text{CuFe}_2\text{O}_4 / \text{SiO}_2$ composite phase.

The observed wide endothermic peak, shown in fig.4, between 313 K and 373 K for the dried gel is attributed to the evaporation of ethyl alcohol, water molecules and other organic residues existing in the sample and it is also confirmed by FTIR. There is no exothermic crystallization peak was observed with in the measured temperature range.

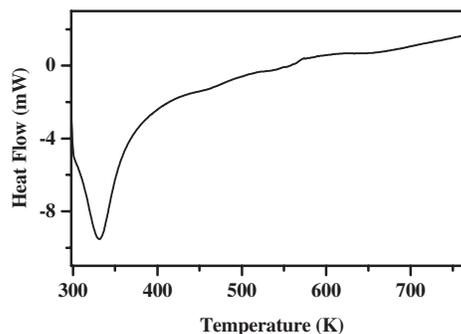


Fig. 4. DSC thermo gram of $\text{CuFe}_2\text{O}_4 / \text{SiO}_2$ nanocomposite

3.1 Transmission Electron Microscopy Results

Fig.5 a & b show the TEM images of the $\text{CuFe}_2\text{O}_4 / \text{SiO}_2$ composite taken at various spots. From Fig.5, the TEM images show the dark particles, CuFe_2O_4 crystals, dispersed uniformly in the white background amorphous SiO_2 phase. From the TEM images, the size of the CuFe_2O_4 crystallites is found to be of order of 10 to 20 nm. Hence, the prepared $\text{CuFe}_2\text{O}_4 / \text{SiO}_2$ compound by sol-gel route is found to be nanocomposite phase.

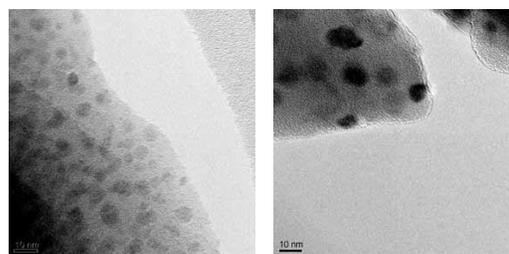


Fig. 5 a&b show TEM images of the $\text{CuFe}_2\text{O}_4 / \text{SiO}_2$ composite taken at various spots

4. Conclusion

Nano-composite containing nano size CuFe_2O_4 crystals dispersed in SiO_2 glass matrix was prepared by Sol-Gel technique. The prepared dried gel heat treated up to 873 K showed only the amorphous phase of SiO_2 . XRD and FTIR results of dried gel heat treated up to 1073 K confirm the formation of CuFe_2O_4 crystals in the SiO_2 amorphous matrix and forms a $\text{CuFe}_2\text{O}_4/\text{SiO}_2$ composite phase. From the TEM images, the size of the CuFe_2O_4 crystallites is found to be of order of 10 to 20 nm. Hence, the prepared $\text{CuFe}_2\text{O}_4/\text{SiO}_2$ compound by sol-gel route is found to be nanocomposite phase.

Acknowledgements

Authors are gratefully acknowledged DRDO, DST and CSIR for utilizing the research facilities available from the major research projects.

References

- [1] J.L. Dorman (Ed), Magnetic Properties of Fine Particles, Fiorani, North Holland, Amsterdam, 1994.
[2] F. Bodker, S. Morup, S. Linteroth, Phys. Rev. Lett. 72 (1994) 282.

- [3] S. Chikazumi, Physics of Ferromagnetism, Clarendon Press, Oxford, 1997, p. 201.
[4] Xiluan Duan, Duorong Yuan, Zhihong Sun, Haiqing Sun, Dong Xu, Mengkai Lv, J. Crystal Growth 252 (2003) 4.
[5] H.M. Gibbs, G. Khitrova, in; H.M. Gibbs, G. Khitrova, N. Peyghambarian (Eds.), Nonlinear Photonics, Springer, Berlin, 1990 (Chapter 1).
[6] A.I. Ekimov, A.L. Efros, A.A. Orushchenko, Solid State Commun. 56 (1985) 921.
[7] R.N. Bhargava, D. Gallenger, X. Hong, A. Nurmikko, Phys. Rev. Lett. 72 (1994) 416.
[8] A.P. Alivisatos, J. Phys. Chem. 100 (1996) 13226
[9] F.H. Dulin, D.E. Rase, J. Am. Ceram. Soc. 44 (1961) 493.
[10] Y.S. Chang, Y.H. Chang, I.G. Chen, G.J. Chen, Y.L. Chai, J. Crystal Growth 243 (2002) 319.
[11] N.N. Parvathy, G.M. Pajonk, A.V. Rao, J. Crystal Growth 179 (1997) 249.
[12] M. Moller, J.P. Spatz, Curr. Colloid. Interface Sci. 2 (1997) 177.
[13] N.F. Borrelli, D.W. Smith, J. Non-Cryst. Solids 180 (1994) 25.
[14] C.J. Brinker, D.E. Clark and D.R. Ulrich, Edited Better Ceramics through Chemistry,
[15] George Socrates, Infrared and Raman Characteristic Group Frequencies Tables and Charts, Third Edition, John Wiley & Sons, 2001.