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Studies on Pure and Divalent Metal Doped Copper Oxide Nanoparticles

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Abstract

Pure and Ni^{2+} doped Copper oxide (CuO) nanoparticles were synthesized by simple solvothermal method. Effect of concentration of the dopant (2.5, 5 7.5 and 10 mole%) on the properties of CuO was analyzed from X-ray diffraction pattern (XRD), SEM, EDAX, UV-VIS, electrical measurements and Photoluminescence spectroscopy . The XRD results clearly indicates that the samples are polycrystalline in nature belongs to hexagonal crystal sturcture and also due to the addition of dopants the average grain size various from 25.14 – 17.5nm. The PL results showed that Ni^{2+} dopant did not give rise to a new PL signal, but it could improve the intensity of PL spectra with a appropriate Ni^{2+} content, which was possibly attributed to the increase in the content of surface oxygen vacancies and defects after doping Ni^{2+}.

1. Introduction

The oxides of transition metals are an important class of semiconductors, which have applications in magnetic storage media, solar energy transformation, electronics and catal-

ysis [1-9]. Among the oxides of transition metals, copper oxide nano particles are of special interest because of their efficiency as nanofluids in heat transfer application [10]. CuO is a semiconducting compound with a narrow band gap and used for photoconductive and photothermal applications [11]. However, the reports on the preparation and characterization of nanocrystalline CuO are relatively few to some other transition metal oxides such as zinc oxide, titanium dioxide, tin dioxide and iron oxide. Also when copper was added as the dopant in other transistion oxide nano particles, it enhances the optical and magnetic properties of the host material [12]. Keeping this in view, in our present study , we made an attempt to prepare copper oxide nanopartilce by simple, cost effective , solvothermal method using microwave irradiation.Ni^{2+} was added as dopant in 3 different mole % viz 2.5 , 5 and 7.5 . The influence of concentration of Ni^{2+} on the structural, optical, and electrical properties of CuO nano crystals was reported herein.

2. Materials and Methods

Analytical reagent (AR) grade copper chloride ($CuCl_2$), urea (NH_2CONH_2) and Nickel chloride ($NiCl_2$) were purchased from Merck Chemicals. These compounds were used without further purification for the preparation of CuO nanoparticles. Copper chloride is mixed with urea in 1:1 molecular ratio. The fine mixture was then dissolved in 100 ml ethylene glycol with vigorous stirring for 60 minute at room temperature and kept in a domestic microwave oven (operated with frequency 2.45 GHz and power 800 W). Microwave irradiation was carried out till the solvent evaporates completely. The colloidal precipitate obtained at the end was cooled to room temperature naturally and washed several times with doubly distilled water and then with acetone to remove the impurities. The sample was then filtered and dried in atmospheric air and collected as the yield. Similarly 2.5 , 5 , 7.5 and 10 mole % $NiCl_2$ was added to above mixture separately for the preparation of Ni^{2+} doped CuO nanoparticles.

Pure and doped CuO nanoparticles were subjected to PXRD analysis. X-ray powder diffraction patterns were obtained using an automated PANalytical X-ray powder diffractometer with monochromated CuK_α radiation (λ=1.540598 AU). The particle size analysis of the as-synthesized materials has been carried out using Scherrer formula. Energy dispersive X-ray analysis (EDAX) was used to estimate the composition of the materials using a Jeol make JSM 5600 LV Model attached with Energy Dispersive Spectrometer of EDAX inc. USA. Optical absorption measurements were done at room temperature using a SHIMADZU UV-2400 PC spectrometer with a medium scan speed sampling interval 0.5 in the wavelength range 200-700 nm. Photoluminescence spectrophotometry was measured on a Perkin– Elmer LS 55 spectrophotometer. The capacitance (C) and dielectric loss factor (tanδ) measurements were carried out to an accuracy of ± 1 % with Agilant 4284A LCR meter in the temperature range of 40 – 150 ºC.

3. Results and Discussion

3.1 Powder XRD Measurement

In order to confirm the material of the grown crystals and to determine the particle size, powder X-ray diffraction (PXRD) data were collected for all the four nanocrystals prepared using an automatedX-ray powder diffractometer (PANalytical) in the 2θ range of 10-70° with CuK_α radiation (λ = 1.54056 Å). Using the observed 2θ (Bragg angle) and d (interplanar spacing), all the reflections were indexed. The PXRD patterns of pure and doped samples were shown in figure 2. The data were indexed following the procedures of Lipson and Steeple . Pure and Ni^{2+} doped CuO nanocrystals belongs to the hexagonal lattice system. No peaks of impurities are found in XRD pattern. The observed PXRD data were indexed by matching with the data available for CuO in the literature (JCPDS file). The XRD data conforms that addition of dopant in CuO lattice doesn't alter its lattice, but it produces slight shift in diffraction peaks, Also the intensity of peaks get suppressed due to dopant addition, which conforms the incorporation of dopant in host lattice. Calculated crystallite size of the prepared samples were given in Table 1, which revealed that, as the concentration of dopant increases, particles size decreases, this may be due to replacement of Cu^{2+} ions by Ni^{2+} ions.

Sample name	Crystallite size (nm)
Pure CuO	25.14
CuO+2.5 mol % Ni	22.15
CuO +5 mol % Ni	19.75
CuO+7.5 mol % Ni	18.32
CuO+ 10 mol % Ni	17.5

3.2 SEM and EDAX Analysis

Figure 2 shows the SEM image of as prepared pure and doped CuO nanoparticles. It shows that the CuO nanoparticles are cubic in shape. As the concentration of Ni^{2+} decreases the size of the cubes, and at the maximum concentration of Ni^{2+} , morphology of the synthesized particle changes drastically into flower like arrangement , this may due to variation in surface atom density of the dopant. The presence of dopant was confirmed by EDAX spectra shown in Figure 3.

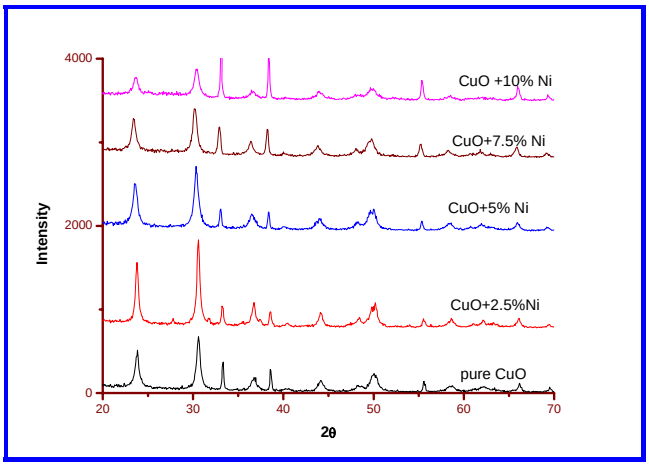

Figure 1: PXRD patterns of pure and doped CuO

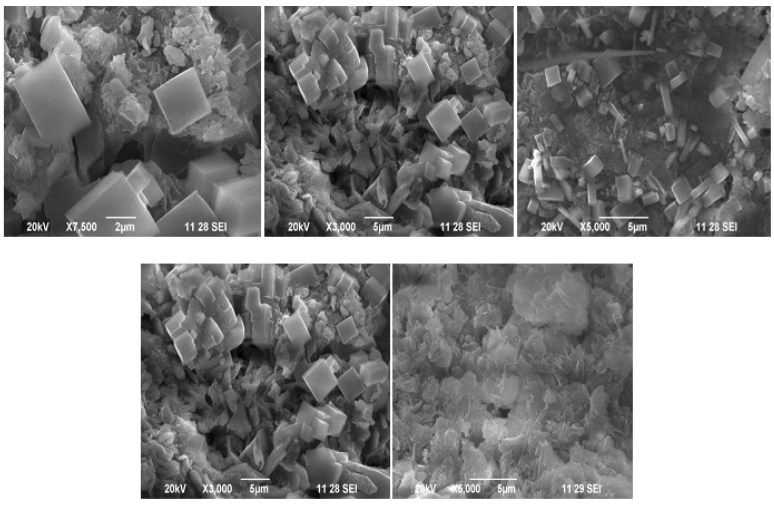

Figure 2: SEM images of pure CuO; Ni^{2+} (2.5, 5.0 , 7.5 and 10 mol %) doped CuO

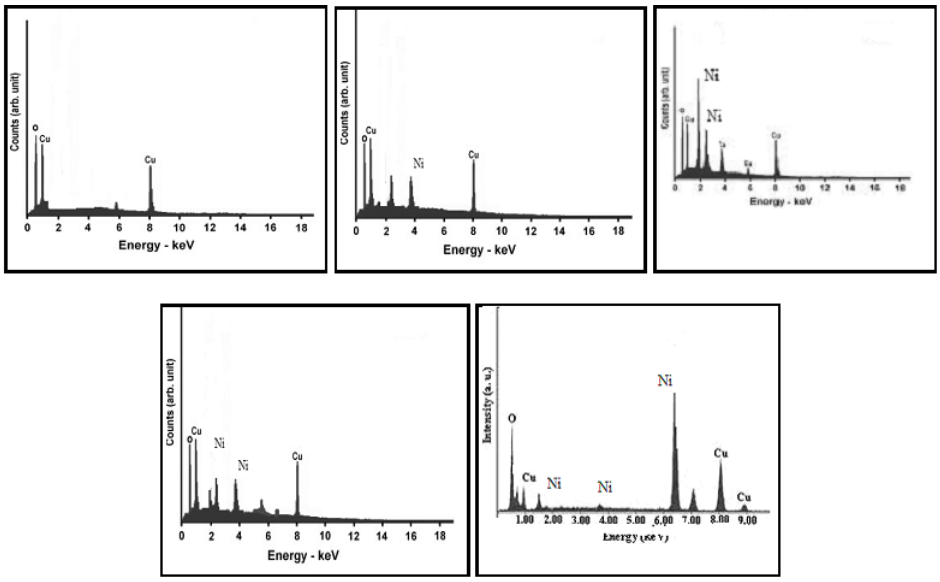

Figure 3: EDAX spectra of pure and Ni^{2+} doped CuO

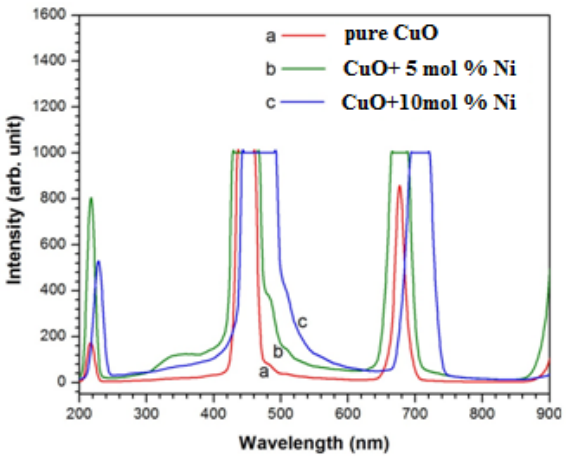

Figure 4: PL spectra of pure , 5mol and 10 mole % Ni^{2+} doped CuO nanocrystals

3.3. PL Analysis

PL emission spectra were recorded for all the synthesized samples. The recorded spectra are shown in Figures 4. All the nanocrystals prepared in the present study exhibit three prominent peaks in the PL spectra and the peaks are observed at around 218, 455 and 674 nm due to (i) band-edge luminescence band and (ii) surface state luminescence bands. The PL spectra indicate clearly that the doping of Ni^{2+} in the host matrix lead to significant changes in PL intensity. However different concentration of Ni^{2+} doping does not bring about new energy levels in the band structure of host CuO to produce new combination of emission. It also indicates that the Ni^{2+} ions substitute for Cu^{2+} ions without formation of other additional energy levels in the host CuO nanocrystals [13].

3.4 Electrical Properties

When the nanostructure material provides a different band structure for the same concentration, one may expect pronounced electric property variation due to changes in the forbidden energy gap [12]. Keeping this in view and also the fact that we have synthesized our materials with very small crystallite sizes (<1.5 nm) using microwave heating technique, we have subjected all the 5 systems considered to DC electrical measurements by using the two probe technique. The observed DC electrical conductivities of nanostructured pure and doped CuO was shown in Figure 6. The DC conductivity over a temperature range 40 to 150ºC is minimum for pure CuO. When Ni replaces Cu sites the conducting ability of the materials seems to have raised, which is maximum for 10 mole % Ni doped CuO. It is generally accepted that smaller the particle size higher the lattice defects. There are reports suggesting that lattice defects form acceptor- or donor-like levels in the forbidden energy gap and act as trapping centers for charge carriers which affect the electrical behaviour [14].

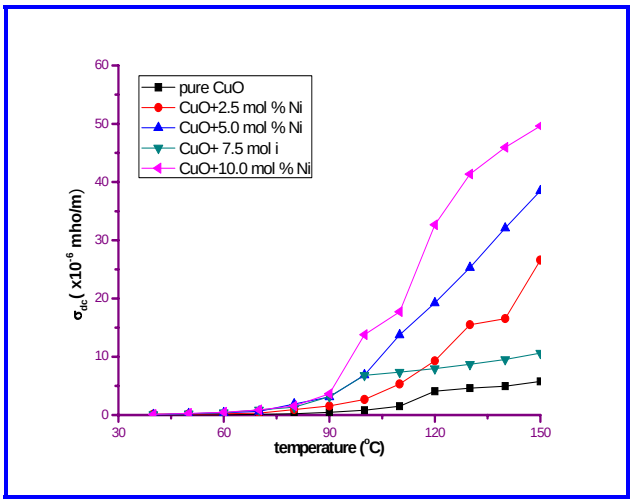

Figure 5: Dc conductivity of pure and Ni doped CuO nano particles

The variation of dielectric constant (ε_r) with frequency at various temperatures (313, 373 and 423 K) for pure and Ni doped CuO nanocrystals are shown in Figure 6. From the Figures it is observed that the ε_r values are decreased with increase in frequency and also ε_r values are increased with increase in temperature from 313 to 423 K. The Ni^{2+} addition decreases the ε_r value at all temperatures and frequencies ranging from 1000 Hz to 1 MHz except in the case of 7.5 and 1 mole % . In these cases it increases the ε_r value.

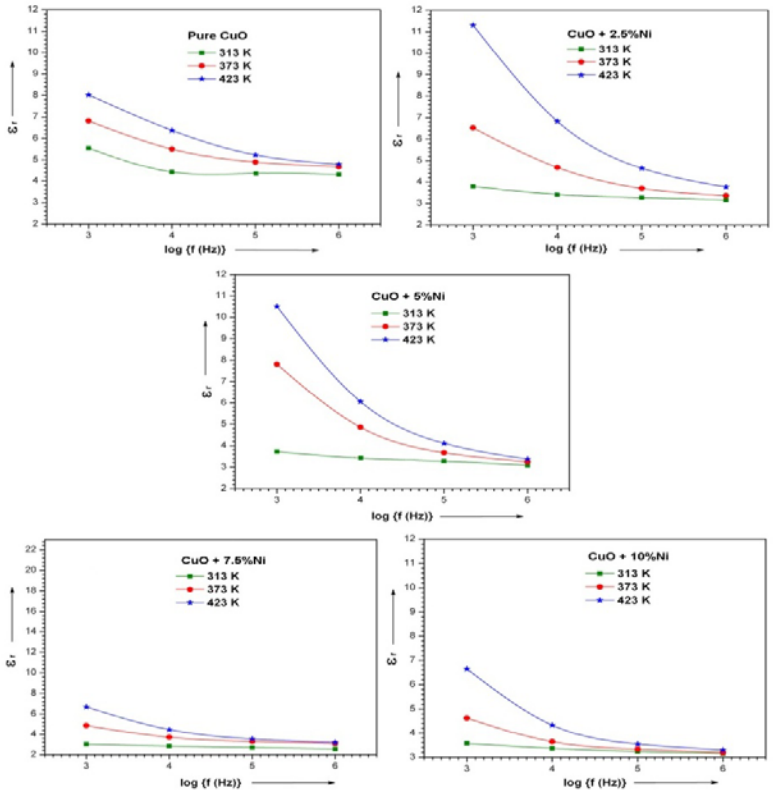

Figure 6: Variation of Dielectric constant with log frequency for various temperature for pure and doped CuO

4. Conclusion

Pure and Ni^{2+} doped (with different concentration viz.,2.5, 5, 7.5 and 10 mole %) CuO nanocrystals were synthesized by simple solvothermal method. The as synthesis materials were conformed by EDAX and PXRD analysis. Nano regimes of the samples were analyzed by SEM and scherrer formula. The results of structural studies revealed that, Ni^{2+} addition decreases the crystallite size with it's increasing concentration. This may be due to replacement of Cu^{2+} ion by Ni^{2+} ions, which has lower ionic radius. Reduction in particle size leads to strong quantum confinement. Also PL results showed that Ni^{2+} additions

doesn't produce any change in energy state , but it leads to change in emission intensity. Also DC conductivity of the doped samples increase with increasing concentration of the dopant than the pure CuO. This may be due to creation of lattice defects due to doping. Thus the doping has significant effect on pure CuO nanocrystals, with doping the physic-chemical properties of cuO was tunned to various levels which find more applications in electronic and photonic industry.

References

[1] A.S. Lanje, R.S. Ningthoujam, S.J. Shrama, R.K. Vatsa, R.B. Pode, Int. J. Nanotechnol., 2010, 7, 979.

[2] E.P. Wolhfarth; Ferromagnetic Materials, Vol. II, North-Holland, Amsterdam, New York, Oxford, Tokyo, 1980.

[3] T. Mitsuyu, O. Yamakazi, K. Ohji, K. Wasa, Ferroelectrics, 1982, 42, 233.

[4] O. Regan, M. Gratzel, Nature, 1991, 353,737.

[5] K. Naazeeruddin, A. Kay, M. Gratzel, J. Am. Chem. Soc., 1993, 115, 6832.

[6] U. Bjoerksten, J. Moser, M. Gratzel, Chem. Mater.,1994, 6, 858.

[7] W.P. Dow, T.J. Huang, J. Catal., 1996,160, 171.

[8] P.O. Larsson, A. Andersson, R.L. Wallengerg, B. Svensson, J. Catal., 1996, 163, 279.

[9] Y. Jiang, S. Decker, C. Mohs, K.J. Klabunde, J. Catal., 1998, 180, 24.

[10] S. Lee, U.S. Choi, S. Li, J.A. Eastman, J. Heat Transfer, 1999, 121, 280.

[11] A.E. Rakhshni, Solid State Electron., 1986, 29, 7.

[12] K. Milenova , I. Stambolova , V. Blaskov , A. Eliyas , S. Vassilev , M. Shipochka, J. Chem tech and Mettalurgy, 2013, 48(3),259.

[13] K. Srinivas, M. Vithal, B. Sreedhar, M.M. Raja, P.V. Reddy, *Journal of Physical Chemistry,* 2009, *C* 113**,** 3543.

[14] R. Sakthi Sudar Saravanan, D. Pukazhselvan, C.K. Mahadevan, J. alloys and compounds, 2011, 509(10), 4065.

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