Int. J. Chem. Sci.: 14(4), 2016, 2433-2438
ISSN 0972-768X
www.sadgurupublications.com

INVESTIGATIONS ON CLHA AND DOPED CLHA NANOPOWDERS BY MECHANOCHEMICAL SYNTHESIS

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ABSTRACT

Semiconductor nanoparticles hold the potential for making more efficient solar cells. Solid-State lighting using LEDs and phosphor material to generate white light is the current research focus in the lighting industry. The present paper describes the investigations of CLHA and different concentrations of 3d-transition metal ions (Mn^{2+}, Fe^{3+}, Co^{2+} and Cu^{2+}) doped CLHA nanopowders were prepared by mechanochemical synthesis. In the case of undoped CLHA nanopowder crystallite size is about 16.15 nm, while doping with transition metal ions crystallite size decreases and then increases with increasing dopant concentration. CLHA nanopowders exhibit white emission with the increase of dopant concentration and are useful for W-LEDs and PDPs.

Key words: CLHA nanopowders, Mechanochemical synthesis, PL and Crystallite size.

INTRODUCTION

The emergent field of nanophotonics deals more particularly with the interaction of optical fields with matter at nano regime. It creates a technological impact, which perhaps cannot match up to any other technological developments that have taken place till date as it deals with every aspect of human life that ranges from building novel materials to medicine. Nanoparticulate thin films possessing desirable electronic properties are of great interest in microelectronics. The uniqueness of nanomaterials lies in its large surface to volume ratio, since nearly all the atoms occupy surface positions. The dependence of specific properties of clusters on their geometrical dimension is termed as quantum size effect and this effect originates from two interrelated causes. As the reduction of grain size to nanometer-dimensions provides increased strength and hardness, super tough and super strong ceramics can be synthesized[1]. These super ceramics can be used in various applications of engineering such as in aerospace and automotive components and high efficiency gas turbines.

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Semiconductor nanoparticles hold the potential for making more efficient solar cells. Solid-State Lighting using LEDs and phosphor material to generate white light is the current research focus in the lighting industry. White LEDs (W-LEDs) will offer high luminous efficiency, energy savings, environment-friendliness, small volume and long persistence compared to conventional incandescent bulbs and fluorescent lamps. Phosphors are the materials, which convert absorbed energy into visible light without going to high temperatures, i.e. incandescence. Rare earth, transition metal ions which usually correspond to electronic transitions within the incomplete 4f and 3d shell stimulate luminescence in phosphors resulting in narrow band spectra.

Usually, phosphors are in the form of crystalline powder with size ranging between 1-100 μm. In order to get high photoluminescence (PL) in nanophosphor particles, large amount of exciting energy should be absorbed by the activator and simultaneously the exciton return to the ground state by radiative process. Methods for improving efficiency of phosphor materials have centred on improving their physical properties by controlling surface morphology, size of phosphor materials and reducing concentration quenching etc. Phosphates are compounds that contain oxyanions of phosphorus (V), ranging from the simple orthophosphate group to condensed chain, ring and network anions. Phosphate structures are generally rigid, resistant to chemical attack, insoluble and thermally stable. This leads to some applications as nuclear waste immobilization hosts or negative thermal expansion materials.

Phosphor layers provide most of the light produced by fluorescent lamps and are also used to improve the balance of light produced by metal halide lamps. Phosphor thermometry is a temperature measurement approach that uses the temperature dependence of certain phosphors for this purpose. The use of labelling or staining agents has greatly assisted the study of complex biological interactions in the field of biology. In particular, fluorescent labelling of biomolecules has been demonstrated as an indispensable tool in many biological studies. The emission of light by a substance not under heat is called luminescence. Chemical reactions, electrical energy, subatomic transitions and crystal stress are some of the causes for this behavior. PL is a process in which a substance absorbs photons and then re-radiates photons. An excitation to a higher energy state and then return to lower energy state accompanied by the emission of a photon is described by quantum mechanics. In emissive displays, all colors are obtained by mixing the three primary colors of red, green and blue at appropriate ratios. The chromaticity of a color can be indicated in color space which is defined according to the convention of the International Commission on Illumination (CIE) in a normalized two-dimensional coordinate system[2].

Hydroxyapatite (HA) is a calcium phosphate bioceramic that belongs to the family of apatites. The apatite family is formed a number of elements characterized by having similar crystallographic structures but not necessarily identical compositions. HA has a specific composition, $Ca_{10}(PO_4)_6(OH)_2$, Ca/P ratio of 1.67 and its crystal structure is hexagonal with a space group $P6_3/m$ (a = b = 0.943 nm, c = 0.688 nm)[3]. The apatite structure is composed of isolated TO_4 tetrahedra. Phosphor materials are prepared by several methods such as high temperature solid-state reaction, mechanochemical, sol-gel, hydrothermal, co-precipitation and emulsion/microemulsion methods. Among these, mechanochemical is an efficient and cost effective method. The chemical processes occurring during mechanical action on solids are more specific and versatile. This method has an advantage for the perturbation of surface-bonded species by pressure to enhance thermodynamic and kinetic reactions. Rao et al. have published their results on different oxide materials, luminescent materials, polymers, glasses and on different drugs in their earlier studies[4-13].

EXPERIMENTAL

The present paper describes the investigations of CLHA and different concentrations of 3d-transition metal ions (Mn^{2+}, Fe^{3+}, Co^{2+} and Cu^{2+}) doped CLHA nanopowders were prepared by mechanochemical synthesis. The structural and surface morphology were carried out by using powder XRD, SEM and TEM techniques. The prepared samples are also characterized by several spectroscopic techniques like Optical absorption, EPR, PL and FT-IR studies.

RESULTS AND DISCUSSION

In the case of undoped CLHA nanopowder crystallite size is about 16.15 nm, while doping with transition metal ions crystallite size decreases and then increases with increasing dopant concentration. At low doping level strain value is large, for that the crystallite size is small. As the dopant concentration increases from 0.01 to 0.05 mol %, the strain values are gradually decreases, hence crystallite size is increased. A small shift is observed in XRD peaks due to the incorporation of transition metal ions into host lattice. In the present study, decrease in dislocation density is observed with increasing transition metal ions concentration accompanied to exponential increase in peak intensity. This is evidence for well crystalline nature of the material. Variation in crystallite size and strain with respective transition metal ions for (a) undoped & 0.01 mol %, (b) 0.03 mol % and (c) 0.05 mol %, respectively is shown in Fig. 1.

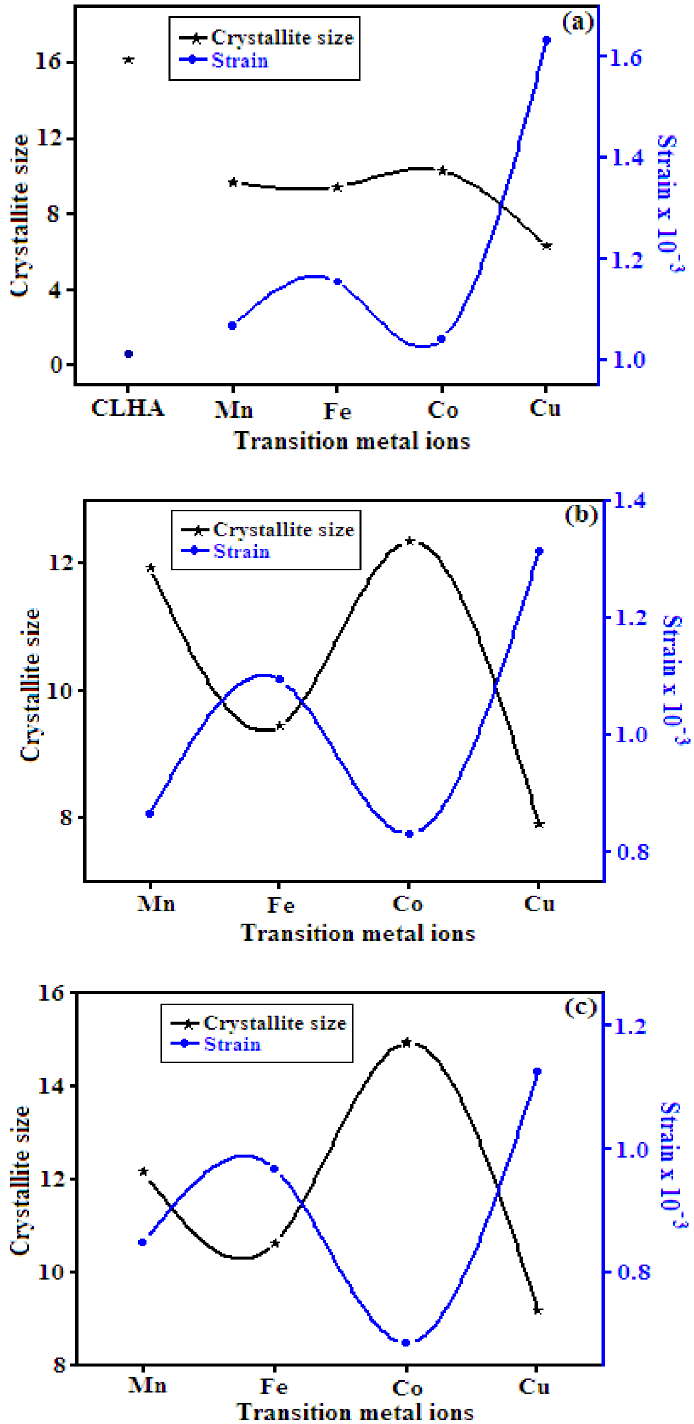

Fig. 1: Variation in crystallite size and strain with transition metal ions

The morphology of prepared samples exhibit stones/sphere like structures indicates that each of them is composed of agglomerates with irregular shape and dimension distributions. It can be seen that by increasing the concentration of transition metal ions, the degree of agglomeration of prepared samples increased. EDS spectra confirms the presence of Ca, P, O and transition metal ions in the prepared phosphor materials. TEM measurements also confirmed the nanocrystalline nature of prepared samples.

From PL data of all prepared CLHA nanopowders, the chromaticity coordinates are calculated and plotted in chromaticity diagram as shown in Fig. 2. Undoped CLHA nanopowder is located in blue-green region, Fe^{3+} and Cu^{2+} doped CLHA nanopowders are located in blue region. In the case of Mn^{2+} doped CLHA nanopowders, emitted color is shifted from yellow to red region as the dopant concentration increases from 0.01 to 0.05 mol % and it may used in lamps and display devices. Co^{2+} doped CLHA nanopowders exhibit white emission with the increase of dopant concentration and is useful for W-LEDs, PDPs.

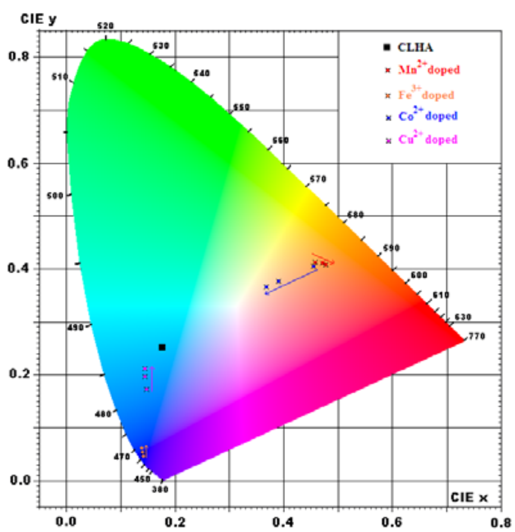

Fig. 2: Chromaticity diagram of undoped and transition metal ions doped CLHA nanopowders

CONCLUSION

The present paper describes undoped and transition metal ions doped CLHA nanopowders by using mechanochemical method and are characterized by different spectroscopic techniques. In the case of undoped CLHA nanopowder crystallite size is about 16.15 nm, while doping with transition metal ions crystallite size decreases and then increases with increasing dopant concentration. TEM measurements also confirmed the nanocrystalline nature of prepared samples. From PL data of all prepared CLHA nanopowders, the chromaticity coordinates are calculated and plotted in chromaticity diagram. CLHA nanopowders exhibit white emission with the increase of dopant concentration and are useful for W-LEDs and PDPs.

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Accepted : 23.09.2016