

NANOCRYSTALLINE RARE EARTH DOPED GARNETS AND THEIR OPTICAL PROPERTIES

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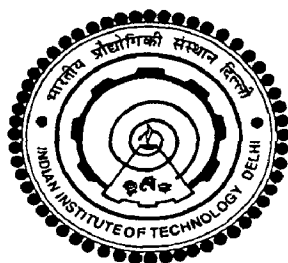
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Department of Chemistry

Submitted

in fulfillment of the requirements of the Degree of
Doctor of Philosophy

to the



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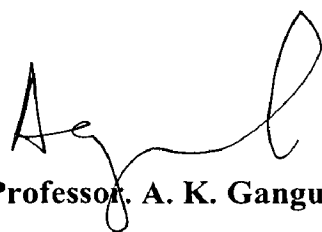
My Son

CERTIFICATE

This is to certify that the thesis entitled, “**NANOCRYSTALLINE RARE EARTH DOPED GARNETS AND THEIR OPTICAL PROPERTIES**”, being submitted by **Mrs. Aditya Verma**, to the Indian Institute of Technology, Delhi for the award of the degree of Doctor of Philosophy in Chemistry, is a record of bonafide research work carried out by her. Mrs. Aditya Verma has worked under my guidance and supervision, and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results contained in this dissertation have not been submitted in part or full, to any other university or institute for award of any degree or diploma.

Date: 1 / 1 / 2013


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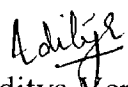
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ABSTRACT

Nanocrystalline oxide materials have gained increasing technological importance with specific attention to the investigation of nanosized oxide particles that can emit light in an efficient and controlled way. These materials can find a wealth of applications in the field of optical materials, spanning from lighting to lasers, solar energy and optical imaging. For this reason, we have chosen a specific class of nanocrystalline oxides, being characterized by interesting features from both a fundamental and an applied point of view. In particular, we have chosen nanocrystalline garnets doped with trivalent lanthanide ions. The motivations for this work is: (1) garnet materials, both in the bulk and in the nanocrystalline form, find numerous applications, as described below, and therefore it is interesting to investigate them; (2) moreover, their chemistry and optical spectroscopy in the bulk form are well known and therefore it is possible to establish meaningful comparisons between the properties of the nanosized and the bulk materials; and (3) finally, garnets are mixed oxides with a definite stoichiometry and therefore the synthetic strategies employed for their preparation are intrinsically more complex than for simple oxides such as Y_2O_3 ; this fact will allow us to discuss in more details the procedures currently employed to synthesize complex nanocrystalline oxides doped with trivalent lanthanide ions (Ln^{3+}). We are focusing on the synthesis, the structural and morphological characterization, and the optical spectroscopy of these materials in powder form.

In chapter 1, a detailed survey of the background literature has been carried out for the state of knowledge existing in the area of garnet based nanocrystalline material doped with different rare earth ions and their optical properties. We have also discussed

synthesis of garnet nanopowder by co-precipitation route and their characterization technique.

In chapter 2, we discuss synthesis, characterization and optical properties of yttrium gallium garnet (YGG) doped with different rare earth ions and their codoping has been presented in this chapter. 2-10 at % Nd: $\text{Y}_3\text{Ga}_5\text{O}_{12}$ and 2 at % Ce: $\text{Y}_3\text{Ga}_5\text{O}_{12}$ and Ce, Nd: $\text{Y}_3\text{Ga}_5\text{O}_{12}$ compounds were synthesized by co-precipitation route. Rietveld refinement studies of x-ray data was carried out on $\text{Ce}_{0.06}\text{Y}_{2.94}\text{Ga}_5\text{O}_{12}$ and $\text{Nd}_{0.06}\text{Y}_{2.94}\text{Ga}_5\text{O}_{12}$ to understand the distribution of dopants in the Y site (dodecahedral) of the cubic $\text{A}_3\text{B}_5\text{O}_{12}$ type structure. Detailed optical study has been carried out on all the compounds and it was observed that there is an increase in intensity with decreasing particle size (as studied in case of Ce: YGG). On codoping Ce and Nd in YGG energy transfer among Ce and Nd ions has been observed.

In chapter 3, we discuss synthesis, characterization and optical properties of Yttrium gallium aluminium garnet nanopowder doped with different rare earth ions has been discussed in this chapter. Synthesis of 2 at % Nd: $\text{Y}_3\text{Ga}_{5-x}\text{Al}_x\text{O}_{12}$ and 2 at % Ce: $\text{Y}_3\text{Ga}_{5-x}\text{Al}_x\text{O}_{12}$ nanopowder by co-precipitation route has been done. Variation in composition and its effect on optical properties has been studied. Nd-doped $\text{Y}_3\text{Ga}_x\text{Al}_{(5-x)}\text{O}_{12}$ (YGAG) materials are investigated for their usefulness as compositionally tuned laser materials while Ce doped series is investigated as phosphor for white LED applications.

In chapter 4, we have discussed effect of substitution of scandium at the octahedral gallium site in the garnet structure to obtain $\text{Y}_3(\text{Sc}/\text{Ga})_5\text{O}_{12}$ (YSGG). Nano crystalline Nd doped yttrium scandium gallium garnets were synthesized by the co-precipitation method. For $\text{Y}_3\text{A}_2\text{B}_3\text{O}_{12}$ (A, B= Ga^{3+}) compounds increase in lattice parameters has been

observed on substitution of Sc^{3+} in place of Ga^{3+} due to larger ionic size of the former as compared to the latter. The thermal decomposition of precursor, crystal phase, microstructure and optical properties of the powders were examined. $\text{Y}_3\text{Sc}_x\text{Ga}_{5-x}\text{O}_{12}$ ($x=2$) has been synthesized by co-precipitation route and found to crystallize in the cubic structure (space group $\overline{\text{Ia3d}}$). The Rietveld refinement of powder X-ray data has been carried out for structural characterization. Cr, Nd codoping in $\text{Y}_3\text{Ga}_{5-x}\text{Sc}_x\text{O}_{12}$ shows that this codoped system can be sensitized by solar radiation.

In chapter 5, we have discussed synthesis of Nd: $\text{Y}_3\text{Sc}_{0.5}\text{Al}_{4.5}\text{O}_{12}$ (Nd:YSAG) by co-precipitation method substituting Sc^{3+} and Al^{3+} for Ga^{3+} in Nd: $\text{Y}_3\text{Ga}_5\text{O}_{12}$ (Nd:YGG). Its phase formation, structure, absorption & photoluminescence (PL) was studied. As Sc and Al replace Ga in YGG, distortion is generated because of size variation of ions. This distortion of polyhedra results in change in crystal field effect as experienced by Nd^{3+} resulting in enhanced Photoluminescence. These substitutions broaden both absorption and emission bands which is believed to be due to inhomogenous crystal field effect caused by Sc addition (larger size than Ga^{3+} , as Al^{3+} and Ga^{3+} are of comparable sizes). Results indicate that Nd:YSAG is a promising material for laser application.

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