Optical study of $MAl_{2-2x}Y_{2x}O_4$ (M = Mg, Ni and Zn) aluminate nanoparticles

*Rohan Samkaria *Sulinder Kalia *Sunil Kumar

*Department of Physics, SMDRSD College Pathankot, 145001 India

Abstract: In the present work, investigations were carried out in order to study the optical properties for a series of $MgAl_{2-2x}Y_{2x}O_4$, $NiAl_{2-2x}Y_{2x}O_4$ and $ZnAl_{2-2x}Y_{2x}O_4$ (x = 0.00, 0.05, 0.07 and 0.10) cubic spinel nanoparticles. All the samples showed optical properties in the ultraviolet wavelength region which results from local environment of cations within the cubic spinel crystal structure. The room temperature optical spectra of different nanoparticles determined by absorption spectroscopy showed that optical band gap increases with an increase in yttrium content.

1. Introduction:

Spinel oxides which has general formula AB_2O_4, where A and B are the divalent and trivalent cations respectively, have received interest due to their structural features which facilitate tailoring of various properties [1]. Among these materials, aluminum based spinels have received attention because of its excellent physical properties such as high melting point, high mechanical strength at elevated temperatures, resistance to radiation damage, low permittivity and low loss tangent. Due to which it has demonstrated potential use for variety of applications.

With the advent of nanotechnology the current research activities on $MgAl_2O_4$ spinel mainly focuses on the improvement of properties through the introduction of suitable dopant and synthesis technique, by reducing dimensions down to the nanoscale. This is primarily because in nanocrystalline materials the physical properties are controlled more by the grain boundaries than by the grains [2, 3]. So the properties of materials in the nanoregime are totally different when compared with their bulk counterparts in the micrometer regime. This modification in the properties upon particle size reduction is attributed to a variety of reasons, namely particle size, shape and

grain boundaries. Because of these modified properties nanostructured materials can be effectively utilized in various applications.

In the recent years nanocrystalline spinel aluminates, MAl_2O_4 (M =, Mg, Ni, Zn) have received considerable interest due to their unique optical properties [4]. These materials exhibit optical bandgap in the ultraviolet region, which allow them to be used as a dielectric and optical material for technological applications [5-7]. In our recent studies, it has been reported that the addition of rare earth yttrium in these nanosized spinel aluminates (i.e. $MgAl_{2-2x}Y_{2x}O_4$, $NiAl_{2-2x}Y_{2x}O_4$ and $ZnAl_{2-2x}Y_{2x}O_4$), strongly influenced their structural and dielectric properties [8-11]. Because of this structural change, it will be interesting to study the optical properties of Y-subsituted aluminum based MAl_2O_4 (M =, Mg, Ni, Zn) cubic spinel nanoaluminates because optical band gap depend crucially on the crystallite size of the material [7].

In this work, we present in detail the optical properties of Y subsituted MAl_2O_4 (M =, Mg, Ni, Zn) nanoaluminates.

2. Experimental:

All the samples were prepared from Merck Germany GR grade chemicals *viz.* *Mg* $(NO_3)_2.6H_2O$, *Ni* $(NO_3)_2.6H_2O$, *Zn* $(NO_3)_2.6H_2O$, *Al* $(NO_3)_3.9H_2O$, *Y* $(NO_3)_3.9H_2O$ and aqueous NH_3 (Merck India, 30%). The samples were prepared by using chemical coprecipitation technique at pH 10.

The synthesis of pure $MgAl_2O_4$ was done by using stoichiometric quantities of $Mg(NO_3)_2{\cdot}6H_2O$ (5.128 g) and $Al(NO_3)_3{\cdot}9H_2O$ (15.005 g) then dissolving them separately in 100mL deionized water and adding simultaneously into a flask containing 200mL deionized water. Ammonia solution was added drop wise till the pH value 10 was attained. The solution was continuously stirred by a magnetic stirrer for 1 h and aged at room temperature overnight. The precipitates were filtered and washed with deionized water and then dried at 120°C for 16 h in a hot air oven. The dried samples were calcined at 950°C in air in a tube furnace programmed at a fixed heating rate of 5°C/min for 8 h.

For the synthesis of pure $NiAl_2O_4$ and $ZnAl_2O_4$ the stoichiometric quantities of Ni $(NO_3)_2 \cdot 6H_2O$ (5.816 g) and Zn $(NO_3)_2 \cdot 6H_2O$ (5.949 g) were used respectively. In addition to this the nanoparticles of $ZnAl_{2-2x}Y_{2x}O_4$ series were calcined at 800°C instead of 950°C. All the other experimental conditions were maintained similar as mentioned above. The yttrium doped derivatives of all the series were prepared by adding the appropriate stoichiometric quantities of dopant salt Y $(NO_3)_3.9H_2O$ and following the same procedure.The optical absorption spectra of the samples were recorded using Perkin Elmer Lambda 750.

3. Results and Discussion:

The absorption spectrum of zinc aluminate particles in transmission mode was recorded by dispersing the particles uniformly in the wavelength range of 200–500 nm. For a direct bandgap semiconducting material the absorption coefficient near the band edge is given by

$$\propto = \frac{A}{h\nu}(h\nu - E_g)^{1/2}$$

where α is the absorption coefficient, hv the photon energy, Eg the energy gap and A is constant depending on the type of transition.

The absorbance spectra of $MAl_{2-2x}Y_{2x}O_4$ (where M =, Mg, Ni, Zn and x= 0.00, 0.05, 0.07 & 0.10) nanoaluminates are shown in Figs. 1-3. From these figures it can be clearly seen that all the samples show broad absorption peaks in the UV region which results from the band to band electron excitations and are related to the energy bandgap in the investigated samples. The band gap was obtained from a linear extrapolation of the absorption edge to the wavelength axis, and is shown in the inset Figs. 1-3, which shows that the band gap energy increases with an increase in yttrium concentration. This type of behavior can be explained by the fact that nanoparticles do not possess a conduction band consisting of a plethora of energy levels but have specific and explicit energy levels. Because of this quantum confinement, the bandgap in nanoclusters increases by an amount

inversely related to the crystallite size [8]. From the structural studies of our previous work it has been confirmed that with an increase in yttrium concentration the crystallite size of $MAl_{2-2x}Y_{2x}O_4$ (M= Mg, Ni and Zn) series decreases [8-10]. Therefore, due to reduction in the crystallite size the electrons excitation among the different energy bands will be hindered as a consequence of which the band gap energy will increase, which is the case for our samples.

Conclusion:

The optical bandgap of all the prepared samples is attributed to the quantum confinement due to small size of the nanoparticles. The optical study showed that band gap energy increases with Y concentration and the reported values suggests a strong potential of these materials for ultraviolet (UV) photoelectronic devices.

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List of Figures:

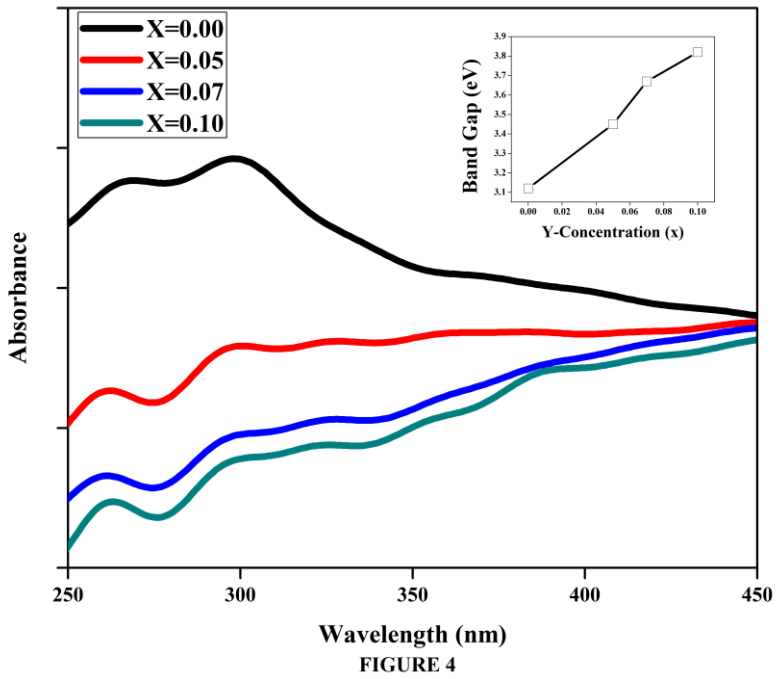

FIGURE 4

Fig.1: Absorbance spectra of $MgAl_{2-2x}Y_{2x}O_4$ (x=0.00, 0.05, 0.07 & 0.10) system. The inset shows energy band gap of the samples.

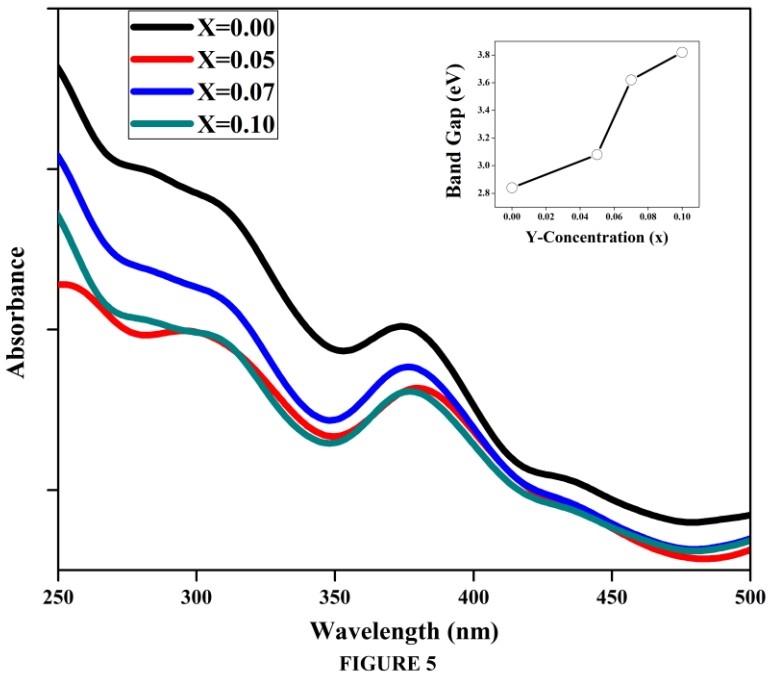

FIGURE 5

Fig.2: Absorbance spectra of $NiAl_{2-2x}Y_{2x}O_4$ (x=0.00, 0.05, 0.07 & 0.10) system. The inset shows energy band gap of the samples.

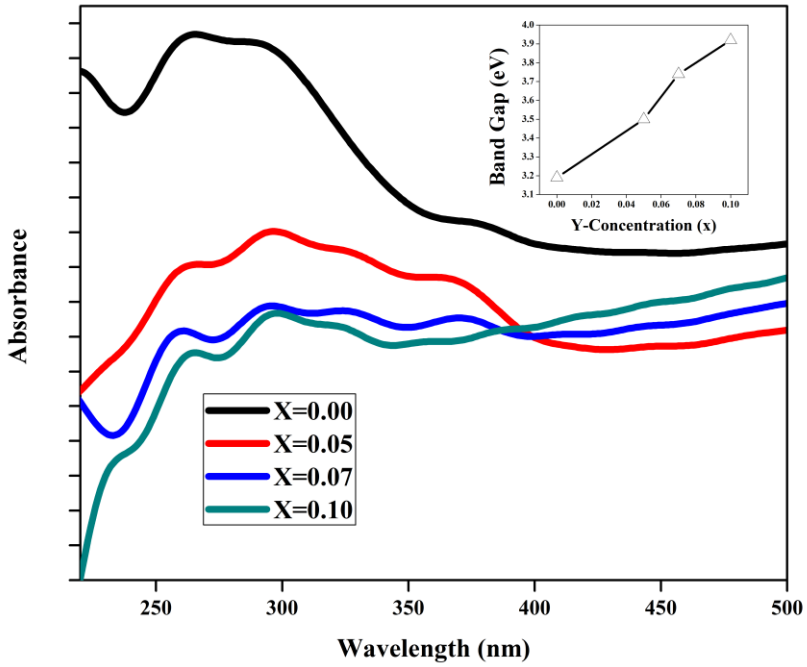

FIGURE 6

Fig.3: Absorbance spectra of $ZnAl_{2-2x}Y_{2x}O_4$ (x=0.00, 0.05, 0.07 & 0.10) system. The inset shows energy band gap of the samples.