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Luminescence Characterization of γ - Irradiated Ce Doped Barium Orthovanadate Phosphors

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Abstract: ***Present paper reports mechanoluminescence (ML), thermoluminescence (TL) and photoluminescence (PL) in γ - irradiated Ce doped barium orthovanadate pohsphors. Barium orhtovanadate and barium metavanadate having different concentration of Ce were prepared by solid state diffusion technique. The ML intensity increases with increasing concentration of dopant and it is found maximum for the sample having 0.1 mol% concentration of Ce. The dependence of ML intensity on γ - dose has also been studied. In TL glow curve of Barium orhtovanadate sample one single peak appears around 120^{0}C. ML and TL spectra contain a sharp peak around 480nm. In the PL of barium orthovanadate a sharp peak at 364nm is obtained along with a broad band around 470 nm. Barium metavanadate shows very weak ML and TL as compared with barium orthovanadate because of less probability of formation of trapped hole centers. The similarity of ML and TL emission suggests that the excitation process is governed by the states of the similar nature.***

Keywords: Mechanoluminescence (ML), Thermoluminescence (TL), Photoluminescence (ML), Solid state reaction

1. Introduction

The alkaline earth metal orthovanadates, $Me_3 (VO_4)_2$ (Me: Ca, Sr, Ba), have attracted much attention owing to their interesting optical, transport and ferroelectric properties [1 - 7]. The intensity of luminescence in $Sr_3 (VO_4)_2$ and $Ba_3 (VO_4)_2$ can be additionally enhanced through the formation of the $Ca_3 (VO_4)_2$ - $Sr_3 (VO_4)_2$ and $Ca_3 (VO_4)_2$ - $Ba_3 (VO_4)_2$ solid solution series [2]. Among them barium orthovanadates exhibit intense rare earth activated luminescence and can be used as luminophors and host materials for lasers [1]. Orthovanadate shows luminescent properties and could be used in television tubes, luminescent lamp coatings and solid state lasers [1 - 3]. Orthovanadates exhibit oxygen ionic conductivity due to the migration of electrons between V^{4+} and V^{5+} centers [8]. Also, intense luminescence can be obtained by tuning the composition in the solid solution series between the isostructural orthovanadates and orthophosphates [8 - 11]. The luminescence and transport properties are determined by point defects and impurity ions whose valance state is different from that ions in a host lattice (e. g. rare - earth elements). The different rare earth containing materials, like orthovanadates and orthophosphates, are useful to assess the extent to which rare - earth ion parameters can be varied and possibly enhanced in various hosts. Using vanadate as host material offers possible solution of these problems due to increased absorption cross sections in rare earth ions [8 - 10].

The ML, TL and PL properties of Ce doped $Ba_3 (VO_4)_2$ and $Ba (VO_3)_2$ have not been systematically studied so far. The present paper reports the ML, TL and PL of these phosphors.

2. Experimental

For the preparation of Ce doped $Ba_3 (VO_4)_2$ phosphors required amount of $BaCO_3$, V_2O_5 and Ce_2O_3 were mixed thoroughly. This was then transferred in a J - mark porcelain crucible and heated in muffle furnace by slowly raising the temperature to about 500^{0}C for 4 hours and cooled to room temperature. Again it was crushed for some time then transferred to a furnace at 550^{0}C for 12 hours then cooled to room temperature. The resulting compound was again crushed and quenched at 550^{0}C for 1hour. γ - irradiation was carried out using a ^{60}Co source. The ML was excited impulsively by dropping a load of 0.4kg onto the sample from the height of 5 cm and luminescence was monitored by PMT connected with the storage oscilloscope. Thermoluminescence glow curves were recorded with the setup consisting of a small kanthal plate, temperature programmer and controller, photomultiplier tube (931 - B), dc amplifier and X - Y recorder. A sample of 2 mg was used every time for recording the glow curves. The ML spectra were recorded using a series of optical band pass filter. Similarly, the photoluminescence spectra of the samples were recorded by using fluorescence spectrometer (SHIMATZU RF - 530 XPC). Emission and excitation spectra were recorded using spectral slit width of 1.5 nm.

3. Results

Fig.1. shows that the time dependence of the ML intensity of $Ba_3 (VO_4)_2$ and $Ba (VO_3)_2$ samples both having Ce concentration of 0.1 mol% at dose level of 1.4×10^3 Gy. Only one peak is observed. The ML intensity of $Ba (VO_3)_2$: Ce (0.1 mol%) is very weak as compared with the ML of $Ba_3 (VO_4)_2$: Ce (0.1 mol%) sample. Similar results have been obtained when the TL glow curves were recorded of these samples

Fig.2. The TL glow curve of $Ba_3 (VO_4)_2$: Ce (0.1 mol%) contains a sharp peak around 120^0C. In TL of Ba $(VO_3)_2$: Ce (0.1 mol%) a weak peak is observed around 80^0C.

Fig.3 shows the dependence of total ML and TL intensity of $Ba_3 (VO_4)_2$: Ce (0.1 mol%) samples for different γ - doses. Initially the intensity increases with increasing γ - doses and seems to saturate above $1.4x10^3$ Gy.

Fig.4 shows the ML and TL spectra of $Ba_3 (VO_4)_2$: Ce (0.1 mol%) samples. It is seen that the peak intensity in ML and TL spectra lies around 480nm.

Fig.5 shows the PL emission spectra of $Ba_3 (VO_4)_2$: Ce (0.1 mol%) samples while it is excited by 247nm. Characteristics emission of Ce^{3+} is observed at 364 nm and around 470 nm.

4. Discussion

Mechanoluminescence and thermoluminescence are most sensitive methods for studying radiation induced effects in the luminescent materials. Non - irradiated undoped and doped $Ba_3 (VO_4)_2$ and Ba $(VO_3)_2$ samples do not show ML. The occurrence of ML in these materials and enhancement of ML and TL with gamma irradiation show the involvement of radiation induced defect centers in ML excitation process. The presence of impurities enhances the probability of formation of defect centers especially if the impurity has a different valence state than the ion it replaces such as RE^{3+} replacing Ba^{2+}. In PL emission luminescence bands at 364 nm and around 470 nm may be attributed to well known 4f – 5d transition of Ce^{3+}. In the ML and TL the emission is centered on 480 nm.

On the basis of experimental results it is suggested that when Ce doped $Ba_3 (VO_4)_2$ is exposed to γ –rays the Ce^{3+} acting as electron trap gets reduced to Ce^{2+} with the production of trapped hole center (VO_4^{2-}) elsewhere. The holes are released on mechanical or thermal excitation. Recombination with electron at Ce^{2+} site leads to the formation of Ce^{3+} in electronically excited state. Luminescence is observed during de - excitation of the excited Ce^{3+} ion. Weak ML and TL of Ba $(VO_3)_2$: Ce show that the probability of formation of trapped hole center is very less in this system.

5. Conclusion

Same states are responsible for both the ML and TL emission in barium vanadates. ML and TL of $Ba_3 (VO_4)_2$: Ce is greater than the ML and TL of Ba $(VO_3)_2$: Ce because of higher probability of formation of trapped hole centers.

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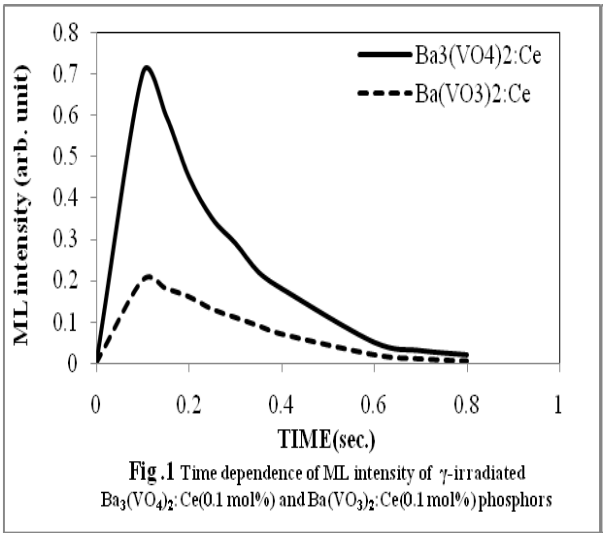

Fig .1 Time dependence of ML intensity of γ-irradiated $Ba_3(VO_4)_2$: Ce(0.1 mol%) and $Ba(VO_3)_2$: Ce(0.1 mol%) phosphors

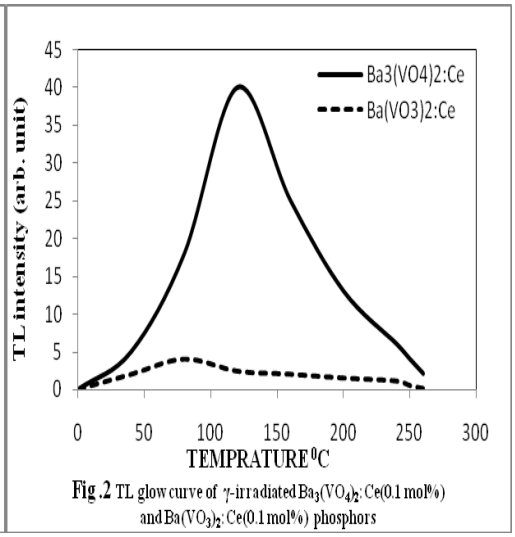

Fig .2 TL glow curve of γ-irradiated $Ba_3(VO_4)_2$: Ce(0.1 mol%) and $Ba(VO_3)_2$: Ce(0.1 mol%) phosphors

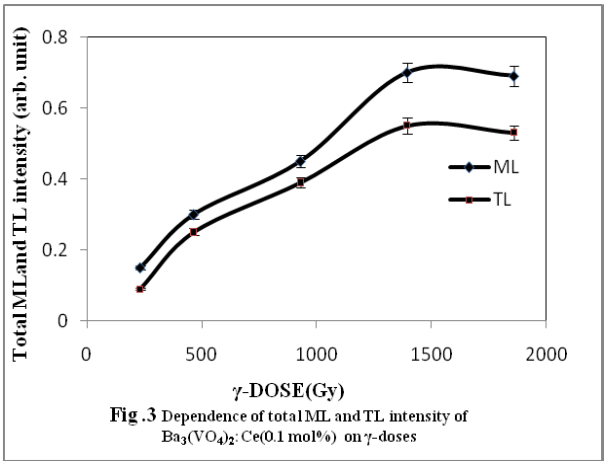

Fig .3 Dependence of total ML and TL intensity of $Ba_3(VO_4)_2$: Ce(0.1 mol%) on γ-doses

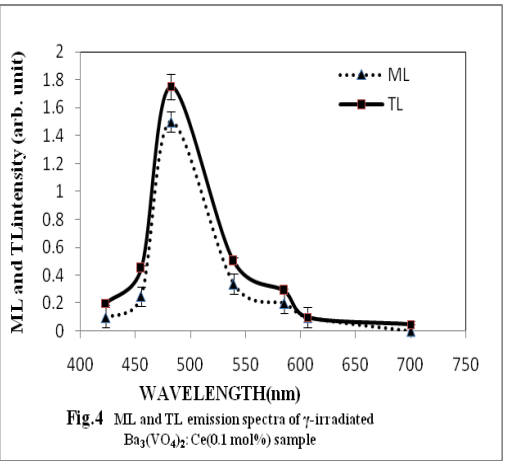

Fig.4 ML and TL emission spectra of γ-irradiated $Ba_3(VO_4)_2$: Ce(0.1 mol%) sample

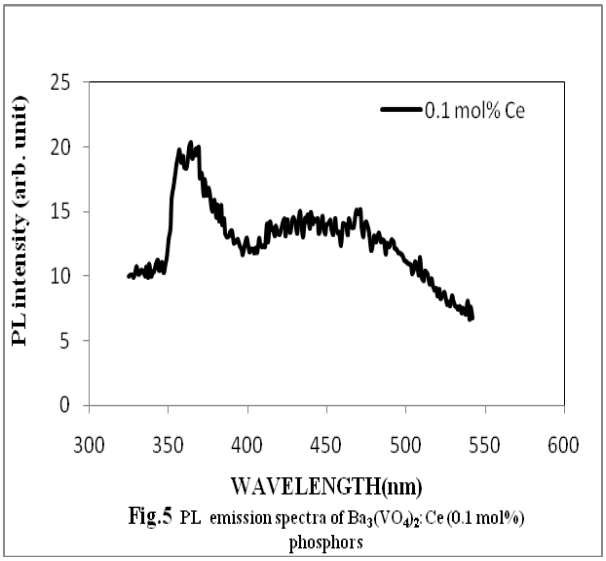

Fig.5 PL emission spectra of $Ba_3(VO_4)_2$: Ce (0.1 mol%) phosphors