Research Paper

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Effect of Fluxing Agent on The Luminescence Properties of Eu2+, Dy3+ Doped Strontium Aluminate Nanophosphors

Physics

KEYWORDS :

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ABSTRACT

Eu2+ doped strontium aluminate phosphors co-doped with Dy3+ were prepared by combustion method. The effect of fluxing agent H3BO3 on structure by viewing physically through photograph, morphology by scanning electron microscope (SEM), mechanoluminescence (ML) and photoluminescence (PL) properties of SrAl2O4: Eu2+, Dy3+ nanophosphors were investigated. The ML intensity for the sample with H3BO3 was found more than the sample without H3BO3, which is due to the reduction in the size of the sample. The PL emission spectra showed broad bands for both the samples. The peak of PL emission spectra showed blue shift for the sample having H3BO3 and was found at 490nm as compared to the sample without H3BO3 at 515nm corresponding to the 4f6 5d1 → 4f7 transition.

Introduction

Materials that present long lasting phosphorescence (LLP) are potential candidates for use in photonics applications, such as display technology and lighting. Among others, strontium based aluminate phosphors are well known for their high quantum efficiency, long-lived afterglow, good chemical stability and other excellent luminescent features, which make them appropriate candidates to replace the traditional II–VI based phosphors (ZnS: Cu,Co). Because metal sulfide system is easy to decompose and turns into black and then lose the luminous character, the applications of conventional phosphors such as metal sulfide compounds are restricted [1–3]. Compared with metal sulfide compounds, the luminescence of flavovirens and blue-green of aluminate system has high performance and the chemical stability [4, 5]. Rare-earth doped long persistence materials have been widely studied due to their many advantages, such as high luminescent brightness, long afterglow time, good chemical stability, and environmental friendliness. Alkaline earth aluminates are one of the best hosts for rare-earth ions [6–11].

Conventional synthesis of strontium aluminate phosphors is the solid-state reaction method, which requires extremely high temperature and a long period of sintering time. As a result, the size of the particles is relatively large and it is difficult to crush the hard phosphor blocks into small particles, which decreases the luminescence intensity. With the development of technologies on materials, several kinds of chemical synthesis techniques have been applied to prepare strontium aluminate phosphors, including chemical precipitation [12], combustion synthesis [13], sol–gel process [14]. The present paper reports the Dy co-doped SrAl2O4:Eu2+ nanophosphors prepared by combustion synthesis. The phosphors were characterized using scanning electron microcopy (SEM). Two samples without H3BO3 and 7.5% of H3BO3 are reported here. The influence of the amount of H3BO3 on the photoluminescence and mechanoluminescence of the prepared nanophosphors are discussed.

EXPERIMENTAL

For preparing powder samples of SrAl2O4:Eu2+, Dy3+, stoichiometric amounts of strontium nitrate [Sr(NO3)2 (99.90%)], aluminum nitrate [Al(NO3)3·9H2O (99.90%)] and urea [NH2CONH2 (99.99%)] were used as raw materials. In addition to it, 2% europium oxide [Eu2O3 (99.99%)] as activators and 4% Dy2O3 as co-activator were dissolved in concentrated nitric acid (HNO3) (99.90%) before transferring them to silica crucible. Boric acid [H3BO3 (99.90%)] is used as the flux while the urea (NH2CONH2) is used as fuel. After the solution is transferred into the crucible with comparatively larger volume, it is placed into a furnace already maintained at temperature of 600oC. Initially, dehydration process was performed by boiling the solution, followed by evolving decomposition under the presence of large amounts of gases (oxides of carbon, nitrogen, and ammonia). Soon the reagent is spontaneously ignited and underwent combustion to produce foamy and voluminous ash. This continues for next few seconds and as it is over, crucible is taken out of the furnace and was kept in open to allow cooling in open atmosphere. The mixture froths and swells forming foam, which ruptures with a flame and glows to incandescence. Upon cooling, we get fluffy form of material, which is then crushed using agate pestle mortar to get the material in the powder form. The whole process was completed within less than 5 min.

The photographs of the as prepared samples were taken. The surface morphology of prepared phosphors were observed by a SEM; (JEOL–JSM-5600) operated at the acceleration voltage of 20 kV. The Photoluminescence (PL) spectra were recorded by Perkin-Elmer LS 45 fluorescence spectrometer using the xenon lamp as excitation source. The ML was monitored by a homemade setup having RCA 931 photomultiplier tube positioned below the lucite plate and connected to a storage oscilloscope (Scientific 300 MHz, SM 340). Loads of constant mass (400gm) was dropped from a particular height. All measurements were carried out at room temperature.

RESULTS AND DISCUSSIONS

Figure 1shows the photograph of as prepared two samples of with and without H3BO3 in the crucible. The sample 'b' contains 7.5% of H3BO3, whereas the sample 'a' does not contain H3BO3 at all. More foamy and voluminous ash was formed in case of 'a'. It was found that the particles in the figure 'a' are slightly bigger than the particles in the figure 'b'. This fact was also confirmed by the SEM and photoluminescence results.

Fig. 1 Photograph of SrAl2O4:Eu2+, Dy3 phosphor with (a) without H3BO3 (b) 7.5% H3BO3

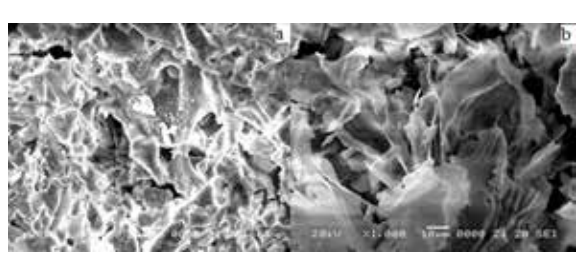

Figure 2 SEM micrograph of SrAl2O4:Eu2+, Dy3 (a) Without H3BO3 (b) With H3BO3

Figure 2a and 2b shows the SEM micrographs of SrAl2O4:Eu2+, Dy3 powder samples without and with H3BO3

respectively. The morphology shows that the grains are multi-sized with number of distinct micro-structural features due to agglomeration of primary nanoparticles. The sample without H3BO3 shows a definite flake like structures with particles in the range 0.5- 3 µm range. In case of the sample with H3BO3 SEM shows similar morphological structure. However upon taking a closer look it shows that the particles are in the size ranging 0.01-0.7µm. Some of the particles could be considered in the nano range one dimensionally.

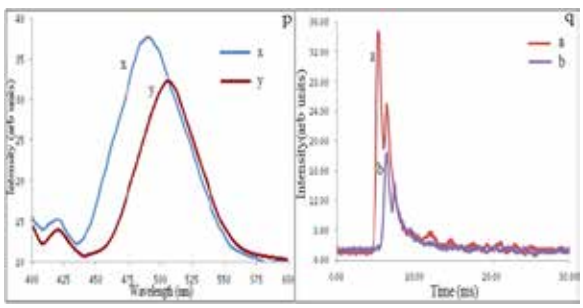

Figure '3p' PL emission spectra, '3q' ML intensity versus time curve of SrAl2O4: Eu2+, Dy3+ phosphors

The emission spectra of SrAl2O4:Eu2+, Dy3+ phosphors at room temperature is shown in Fig. 3p. The emission spectra of the powder samples without and with H3BO3 are shown by 'y' and 'x' respectively. At 365 nm excitation the broad emission band spectra are observed for both the cases. Two peaks were recorded for both the samples. The position of the first peak was found nearly same for both the sample whereas the second peak recorded for the sample with H3BO3 at 490nm showed blue shift as compared to the peak observed at 515 nm for the sample without H3BO3. The blue shift in the emission spectra is due to quantum size effect [15]. The intensity of the sample 'x' is more than sample 'y', which is due to the reduction in the size of the sample. The broad emission peak at 490nm is due to the transition of Eu2+ from the excited state of 4f6 5d1 configuration to the ground state 4f7. Photoluminescence spectrum confirms that the emission does not arise from the co-activator ions, suggesting that the defect centers are due to Eu2+ ions acting as trap levels in bringing out various emission features.

Mechanoluminescence is an important physical phenomenon where an emission of light is observed due to mechanical deformation of materials, due to some mechanical stress. In the present ML studies, an impulsive deformation technique has been used. During the deformation of a solid, a great number of physical processes may occur within very short time intervals, which may excite the process of photon emission. When a load is applied on to the phosphor, initially the ML intensity increases with time, attains a peak value and then it decreases with time. Such a curve between the ML intensity and deformation and post-deformation time of a solid is known as the ML glow curve.

Fig 3q shows the characteristics curve between ML intensity versus time of SrAl2O4:Eu2+, Dy3+ phosphors without H3BO3 'b' and with H3BO3 'a' respectively. The height of the falling piston was 50cm for both the sample. The mass of the cylindrical shape piston was 400gm. During ML measurement, the quantity of samples in both the cases was kept constant. Two peaks were seen in the ML response, the first peak is the transient response of the pressure exerted on the sample whereas the second peak is related to the electrons captured in the shallow traps. The presence of two peaks indicates that some charge transfer is involved in the ML process, which could be explained on the basis of piezoelectrically induced detrapping model of ML. The intensity of the sample 'a' is more than sample 'b', which is due to the reduction in the size of the sample. This shows that an important role to reduce the size of the particle has been played by the fluxing agent H3BO3.

Conclusions

The present work was motivated to determine the exact role of H3BO3 on the phosphorescence characteristics of SrAl2O4: Eu2+ phosphors co-activated with Dy. SrAl2O4: Eu2+, Dy3+ nanophosphors were successfully synthesized by the combustion method using H3BO3 as the flux. The SEM micrographs showed flake type structure for both the samples with varying crystallite sizes. H3BO3, as a fluxing agent, has medium function and promotes rare earth ions entering into matrix lattice. It was found that it could control the particle size, reduce the sintering temperature and change the luminous performance of the phosphors. It does not made significant changes to the morphology of the nanostructures. The ML intensity – time graph showed two peaks. Brighter ML peak was recorded for the sample of SrAl2O4: Eu2+, Dy3+ having H3BO3 as compared to the sample without having H3BO3. These properties indicate that this sample can be used as sensors to detect the stress of an object and self-diagnosis applications. A broad emission peak having blue shift in the PL emission spectra for the sample of SrAl2O4: Eu2+, Dy3+ having H3BO3 as compared to the sample without having H3BO3 was seen which is due to quantum size effect.

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