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Effect of Eu doping concentration on Mechanoluminescent (ML) properties of MAl_2O_4 (M=Ba, Mg)

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Abstract

Mechanoluminescence (ML) is the phenomenon of light emission from certain materials when subjected to any mechanical actions like striking, grinding etc. Undoped and Eu doped samples of MAl_2O_4 (M=Ba,Mg) were prepared via high temperature solid state reaction route. The phase formations and surface morphologies of Eu doped powder samples were studied by taking XRD and SEM. ML studies of undoped and Eu doped samples were conducted by impact method. Among the undoped samples significant ML emissions were observed only from barium aluminate. Significant variations in ML emission properties of barium aluminate and magnesium aluminate were observed after doping with Eu and optimum Eu concentration values were identified in each case. The samples were irradiated with gamma and corresponding variations in ML intensities were studied. Photoluminescence (PL) emission properties of Eu doped samples were studied by taking PL spectrum.

Key words: Mechanoluminescence, XRD, SEM, gamma irradiation, Photoluminescence

Introduction

Mechanoluminescence (ML) is the phenomenon of light emission from certain materials when subjected to any mechanical actions like striking, grinding etc [1]. Recently a search for mehanoluminescent smart materials found a great attention due to its immense applications in the field of stress sensing [2],ML paint systems [3],crack detection [4],earth quake monitoring [5] etc. Among various systems ,aluminates are found to be promising hosts for ML activity especially rare earth doped strontium aluminates.For the last few years a lot of works were

reported on the ML activity of europium, dysprosium doped strontium aluminates [6,7,8,9]. Besides strontium aluminates, Barium aluminates and magnesium aluminates are also two potential and commercially important systems of this class. Barium aluminate belongs to stuffed tridymites with high dielectric, pyroelectric and mechanical properties [10]. Magnesium aluminate spinel shows high hardness, high mechanical strength, low thermal expansion coefficient and high resistance against chemical attack [11]. Inspite of having so many industrially compatible properties very limited studies were conducted to understand about the mechanoluminescent properties of the barium and magnesium aluminates. To the best of our knowledge no systematic works were reported till to the date on ML property of unirradiated europium doped magnesium aluminates. The main interest of the present study is to understand about the mechanoluminescent properties of barium and magnesium aluminates in the absence and presence of europium ions.

Experimental

Stoichiometric weights of 99.99 % $BaCO_3$, $C_4Mg_4O_{12}.H_2MgO_2.xH_2O$, Al_2O_3, Eu_2O_3 were used as starting reagents for the synthesis of required compositions. The reagents were thoroughly grinded for two hours using double distilled water as mixing medium. The well grounded mixture was dried at 100°C and calcined in air atmosphere at 1150°C for 2 hours. The product obtained after calcination was used for further characterization studies. The phase formations of the samples were confirmed by taking powder X-ray diffraction analysis (XRD) [Model D8 Advance Antonn Paar,TTK450 using Cu X-ray source (λ=1.5406 Å). Surface morphology and particle size of the samples were studied using SEM analysis (model JEOL Model JSM-6390LV) of the respective samples. Mechanoluminesene (ML) studies of the samples were conducted via impact method [12]. Photoluminescence studies of the samples were carried out using PL apparatus (Horriba Flurolog spectroFlurometer).

Results and discussion

The powder XRD patterns shown in fig 1 (a) and (b) are well matched with the peaks mentioned in ICDD card numbers 17-0306 and 75-0905 that indicated the phase formations of the phosphor powders. SEM analysis of sample powders showed that undoped barium aluminates consist of irregular shaped particles with agglomerations in which particle size varies from 10 to 20 micrometers (Fig 2a) and no significant variations were observed after doped with europium (Fig 2b).But the surface analysis of Eu doped magnesium aluminates indicates that grains mostly possess disc shaped morphology having grain sizes less than 10 micrometers and seldom agglomerations were observed (Fig 2c).

Mechanoluminescence (ML) Studies

The mechanoluminescence studies of undoped samples of barium and magnesium aluminates were conducted and significant mechanoluminescence emissions with single emission peaks were observed only from barium aluminates. The ML emissions in the absence of rare earth impurities can be attributed to the intrinsic type mehanoluminescence properties of barium aluminates [13]. The time taken to attain ML peak intensity (t_m) was found to be 150 ns (Fig 3).After doping the samples with europium, magnesium aluminate became ML active along with significant enhancements were observed in the ML emission intensities of barium aluminates. The presence of Eu ions increases the density of traps or concentration of electron-hole pairs during fracture also increases [14].During the impact of the load on the sample charges of opposite nature will be developed on the either surfaces of the fractured surfaces which produces an intense electric field. Electrons from the negatively charged surfaces gets accelerated due to influence of this high order of electric field and their impact on positively charged surfaces excites the luminescence centers and recombination luminescence may be produced. But sometimes the probability of tunneling of electrons decreases if the variation of interatomic electric field is uniform. In that cases origin of ML can also be due to the tunneling of electrons due to the movement of charged dislocations [12].Due to Eu doping slight variations in t_m were observed in both systems. In $BaAl_2O_4$:0.05 Eu and $MgAl_2O_4$:0.05Eu the value of tm was found to be as 250ns and 300ns respectively. As europium doping concentrations were increased in steps significant variations were observed in ML emission intensities.Intially ML intensity rises with Eu concentration and showed maximum intensities at 0.05 mole% in both aluminates. Beyond that concentration ML intensities of both samples decreased considerably and at 0.3 mole % ML intensity totally vanishes in magnesium aluminates. The decrease in ML intensity at higher dopant concentrations can be due to the decrease in distance between free charge carriers at higher doping concentration that results in energy transfer between free charge carriers and so luminescence decreases [14].Significant rises in ML emission intensities were observed in both $BaAl_2O_4$:0.05 Eu and $MgAl_2O_4$:0.05 Eu with increase in impact velocities (Fig 4-6). This can be due to the increase in rate of creation of new surfaces during impact [15].Only negligible variations were found in the value of t_m of each system due to increase in impact velocities and doping concentrations.

Photoluminescence (PL) Studies

The PL emission spectrum of Eu doped barium aluminate and magnesium aluminates were showed in fig 7(a) and (b). A broad emission spectrum in the range 450nm to 600 nm peaking around 500 nm were observed in the emission spectrum of $BaAl_2O_4$:Eu.The broad emission can be due to the $4f^65d^1 \rightarrow 4f^7$ transitions of Eu^{2+}.The oxidation state of added Eu ion can be +3 and samples were prepared in air atmosphere. But the presence of broad emission indicates that most of added Eu^{3+} is reduced to Eu^{2+} in barium aluminate host. But in the case of Eu doped magnesium aluminates prominent emissions in 592 nm and 613nm can be due to the characteristic transitions (5d→7f) of Eu^{3+} [12]. Thus in the case of magnesium aluminates no reduction mechanisms were observed as in barium aluminates.

Conclusions

Undoped and europium doped samples of barium and magnesium aluminates were synthesized via high temperature solid state reaction in air atmosphere. Only barium aluminates exhibited significant ML emissions in undoped form. Significant ML variations were observed in both samples of barium and magnesium aluminates after doping with europium. Variations of ML intensities were observed with dopant concentrations and highest ML emissions in both systems were identified as 0.05 mole %. Also a linear rise in ML intensity was observed in all systems with rise in impact velocities.

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