

## Combustion Synthesis of UV Emitting Mn<sup>2+</sup> Doped Nano-Crystalline Calcium Borate.

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**ABSTRACT:** Metal borates have excellent mechanical properties, good chemical inertness and high stability at high temperature, lightweight, and low thermal expansion coefficients. This paper explains the synthesis of calcium borate doped with Mn<sup>2+</sup> by solution combustion method, which is one step process carried out at low temperature, with different concentration of activator and its effect on the photoluminescence intensity at different excitation wavelengths. Ca<sub>2</sub>B<sub>2</sub>O<sub>5</sub>:Mn<sup>2+</sup> shows excellent UV emission and is a potential candidate for UV light sources. The structural properties and morphology were studied by XRD. The photoluminescence properties of the phosphor (excitation and emission) were studied at room temperature. It was observed that the excitation intensity decreases with increasing concentration of Mn, for emission at 339 nm & 350 nm. The emission spectra were observed for excitation wavelength of 254 nm. The maximum emission intensity was observed for 1 m% concentration of Mn doped sample. The emission intensity decreases with increase in doping concentration.

**Keywords** - Combustion synthesis, Concentration quenching, metal borate, UV emission

### I. INTRODUCTION

Borate compounds are well known remarkably for their use in industries and mineralogy. Metal borates have excellent mechanical properties, good chemical inertness and high stability under high temperature, lightweight, and low thermal expansion coefficients. Ma *et al* [1] synthesized aluminium borate ceramic microtubes with open ends having a variety of promising applications such as being filled with other materials for protection or for the fabrication of novel composites or filtering media. Li R *et al* [2] synthesized single-crystalline barium polyborate Ba<sub>3</sub>B<sub>6</sub>O<sub>9</sub> (OH)<sub>6</sub> (BBOH) Nano rods using a low temperature, organic-free hydrothermal technique. It was found that β-BaB<sub>2</sub>O<sub>4</sub> (BBO) nanospindles can be achieved by annealing the BBOH nano rods at a relatively low temperature of 810 °C. Calcium borate is a potential material for applications in ultraviolet (UV) light sources, light emission diodes (LEDs), and luminescent phosphors, ceramic coatings, glass fibres and dielectric devices. Zhao *et al* [3] synthesized thorn-like polycrystalline Ca<sub>2</sub>B<sub>2</sub>O<sub>5</sub>·H<sub>2</sub>O microspheres with nano-sized slices using boric acid and calcium hydroxide as reactants by a facile catalyst-free hydrothermal method at low temperature. Hao and Gao *et al* [4] showed that calcium borate doped with europium is a blue phosphor which can be used at temperatures suitable for glass substrates in flat panel applications. They developed thin films of CaB<sub>2</sub>O<sub>4</sub>:Eu on glass substrates by spray pyrolysis. Blue cathodoluminescence was observed and explained by an electron transfer mechanism. Ishii *et al* [5] observed that by adding a small volume of calcium borate as a flame retardant, the flammability of the epoxy moulding compound can be decreased and calcium oxide in the calcium borate accelerates the curing reaction of epoxy compounds due to its absorption of water from the phenolic resin hardener. Calcium borate whiskers with highly thermal stability were synthesized by hydrothermal method by Song *et al* [6]. It has been revealed that lanthanum calcium borate (La<sub>2</sub>CaB<sub>10</sub>O<sub>19</sub>) crystals show two-photon absorption (TPA) induced by a UV laser field by Kitek *et al* [7]. Majcrowski *et al* [8] established that intensity of the Nd emission line at 910–930 nm is changed inversely after studied structural, dielectric, and optical properties of yttrium calcium borate glasses and addition of Yb to the Nd doped crystals La<sub>2</sub>CaB<sub>10</sub>O<sub>19</sub>. Absorption and emission spectra of Nd: Yb: La<sub>2</sub>CaB<sub>10</sub>O<sub>19</sub> single crystals at different impurity content and temperatures were observed. Santos [9] showed that calcium borate glasses are potential candidates for optical applications due to their ease of shaping as large bulk samples or fibres. Alkaline earth borate Sr<sub>2</sub>B<sub>2</sub>O<sub>5</sub> doped with Tb<sup>3+</sup> was prepared by Rong Wang *et al* by using conventional solid state method and characterized by XRD and photoluminescence properties. The concentration quenching mechanism was also studied. Bright green emission centered at 545 nm corresponding to the <sup>5</sup>D<sub>4</sub> → <sup>7</sup>F<sub>5</sub> transition of Tb<sup>3+</sup> was observed [10]. In PLLCD as a backlight, a narrow band, near UV emitting source is required with a peak emission wavelength close but not extending into the visible region. Any visible emission is undesirable since it will change the screen colours. A phosphor with narrow emission band around 390 nm is desirable, since at this wavelength the transmission of standard glass, polarizing plastic, other coating and LCD materials is at acceptable level. Ca<sub>2</sub>B<sub>2</sub>O<sub>5</sub>:Mn<sup>2+</sup> shows such a near UV emission. To the best of

our knowledge alkaline earth borate Ca<sub>2</sub>B<sub>2</sub>O<sub>5</sub>:Mn<sup>2+</sup> is not synthesized by solution combustion method which is one step process carried out at low temperature. This paper explains the synthesis of nanocrystalline calcium borate doped with Mn<sup>2+</sup> with different concentration of activator and its effect on the photoluminescence intensity at different excitation wavelengths and shows that as prepared phosphor is a potential candidate for UV light sources.

## II. EXPERIMENTAL

The starting AR grade materials (99.99% purity), taken were Ca<sub>2</sub>NO<sub>3</sub> (99.99%) and Boric Acid H<sub>3</sub>BO<sub>3</sub> (99.99%). Urea (NH<sub>2</sub>CONH<sub>2</sub>) was used as fuel for combustion and Ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>) was used as oxidiser. MnSO<sub>4</sub>.H<sub>2</sub>O (99.99%) was taken for doping manganese. In the present investigation, material was prepared according to the chemical formula Ca<sub>2-x</sub>B<sub>2</sub>O<sub>5</sub>: xMn (x = 0.005, 0.01, 0.02 and 0.05). For combustion 5 mol % of urea to the total nitrate mixture was used. All the precursor materials taken in their stoichiometric ratios as shown in Table 1 were put in the agate mortar and mixed well for half an hour.

TABLE 1 THE BALANCED MOLAR RATIOS OF PRECURSORS

Product	Corresponding reaction with balanced molar ratios of precursors
Ca <sub>2</sub> B <sub>2</sub> O <sub>5</sub> :Mn <sup>2+</sup>	(2-x)Ca(NO <sub>3</sub> ) <sub>2</sub> .4H <sub>2</sub> O + 2H <sub>3</sub> BO <sub>3</sub> + 5NH <sub>2</sub> CONH <sub>2</sub> + 5NH <sub>4</sub> NO <sub>3</sub> + x MnSO <sub>4</sub> .H <sub>2</sub> O → Ca <sub>2</sub> B <sub>2</sub> O <sub>5</sub> :Mn <sup>2+</sup> + Gaseous products (H <sub>2</sub> O, NH <sub>3</sub> and NO <sub>3</sub> etc) [x=0.005,0.01,0.02,0.05]

The required amount of double distilled water was added to the precursor material to get a paste-like consistency. The paste was mixed well for homogenization of the mass. The paste was then kept in the quartz container and placed in a muffle furnace maintained at around 400–600 °C. In about 2-3 minutes reaction started with bright yellow flame. The reaction continued only for a few seconds. As soon as the reaction was over, quartz container was taken out of the furnace and allowed to cool. The as prepared phosphor was then grind to fine powder and heated at 800 °C for 2 hours in a reduced atmosphere of carbon. The X-ray diffraction (XRD) technique was used in order to identify the product and check its crystalline nature.

## III. RESULTS AND DISCUSSION

Fig. 1 shows the X-ray diffractogram of Ca<sub>2</sub>B<sub>2</sub>O<sub>5</sub>:Mn<sup>2+</sup>. The X-ray diffractogram was matched with JCPDS file no. 79-1516 in order to identify the product and check its crystalline nature. Structure was characterized by XRD pattern using XPERT-PRO Pananalytical diffractometer with Cu Kα radiation (λ = 1.5405 Å) operating at 40 kV, 30mA. The peaks of (211), (004), (-211), (210), (014) and (115) planes, which characterize Ca<sub>2</sub>B<sub>2</sub>O<sub>5</sub> crystal were obtained.

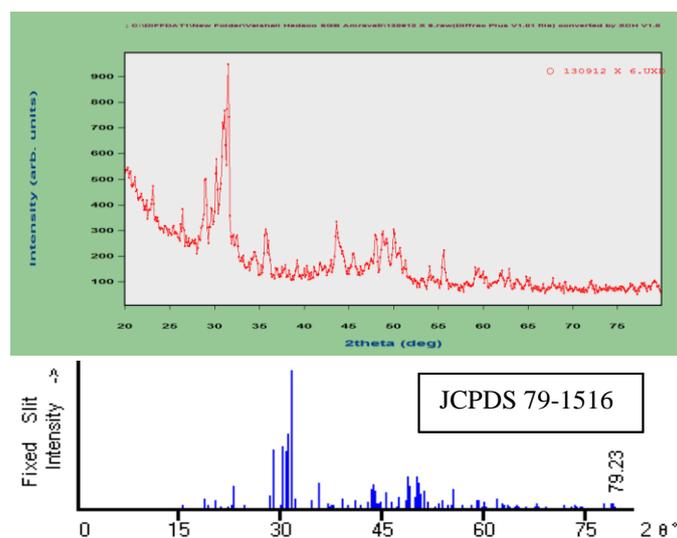


Figure 1. XRD diffractogram of Ca<sub>2</sub>B<sub>2</sub>O<sub>5</sub>:Mn<sup>2+</sup>

The crystallite size was calculated by using Debye-Scherrer formula by broadening of the major peak at 2θ = 31.50° as shown in Fig 2. The crystallite size was calculated as follows:

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The major peak is at  $2\theta = 31.50^\circ$ . Hence  $\cos \theta = \cos (15.75^\circ) = 0.9624$

$FWHM = B = 0.99^\circ = 0.99 * 2\pi / 360 = 0.01727$  radians

According to Debye-Scherrer Formula [11],

Crystallite size T is given by

$T = 0.9 * \lambda / B (\text{rad}) \cos \theta$

Using values of B and  $\cos \theta$ ,

$T = 0.9 * 0.154 \text{ nm} / 0.01727 * 0.9624 = 8.33 \text{ nm}$ .

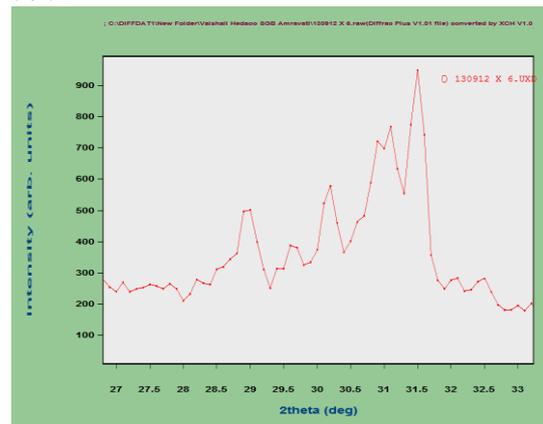


Figure 2. Major peaks of Ca<sub>2</sub>B<sub>2</sub>O<sub>5</sub>:Mn<sup>2+</sup> XRD

The photoluminescence properties of the phosphor (excitation and emission spectra) were observed using Hitachi F-7000 Fluorescence Spectrophotometer at room temperature. The slit width of 5 nm was kept. The photoluminescence excitation spectra of the samples for emission at 339 nm & 350 nm are shown in Fig. 3 (a) & (b). The excitation spectra were checked for different emission wavelengths 339 nm and 350 nm. It was found that there was not any significant difference in intensities for two different emission wavelengths. The excitation spectra were also checked for different concentration of Mn. It was observed that the excitation intensity decreases with increasing concentration of Mn. The samples were prepared by taking 0.5 m %, 1 m %, 2 m % and 5 m % of Mn dopant concentration in Ca<sub>2</sub>B<sub>2</sub>O<sub>5</sub> host. The excitation spectra shows maximum excitation intensity for 1% Mn sample and concentration quenching was observed for higher doping concentration of Mn. Moreover, the intensity was observed not to be affected with further increase in the concentration of Mn. The concentration quenching effect can be explained as follows:

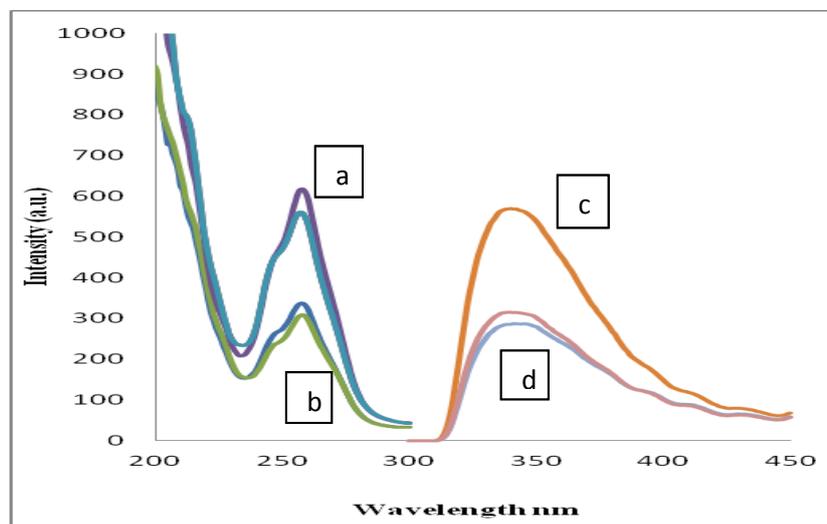


Fig 3 photoluminescence spectra

Excitation spectra:

- (a) Ca<sub>1.99</sub>B<sub>2</sub>O<sub>5</sub>: 0.01Mn at  $\lambda_{em} = 339 \text{ \& } 350 \text{ nm}$
- (b) Ca<sub>2-x</sub>B<sub>2</sub>O<sub>5</sub>: xMn ( $x=0.02, 0.05$ ) at  $\lambda_{em} = 339 \text{ \& } 350 \text{ nm}$

Emission spectra:

- (c) Ca<sub>1.99</sub>B<sub>2</sub>O<sub>5</sub>: 0.01Mn at  $\lambda_{ex} = 254 \text{ nm}$
- (d) Ca<sub>2-x</sub>B<sub>2</sub>O<sub>5</sub>: xMn ( $x=0.02, 0.05$ ) at  $\lambda_{ex} = 254 \text{ nm}$

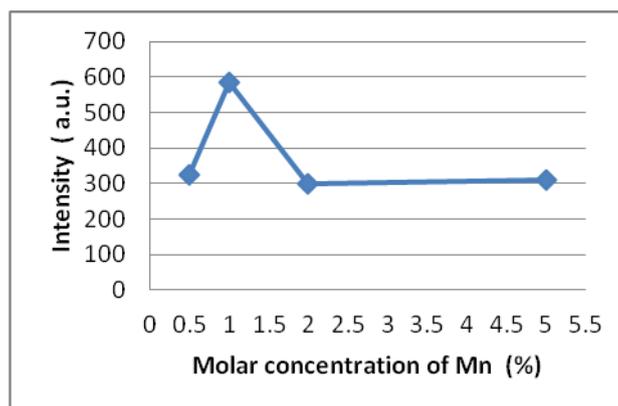


Fig 4. Concentration quenching of  $Ca_2B_2O_5:Mn^{2+}$

In principle, if there is an increase in concentration of the lanthanide ions in a given material it should be accompanied by an increase in the emitted light intensity, but it has been established that such behavior occurs up to a certain critical concentration [12]. Above this critical concentration the luminescence intensity starts to decrease. This process is known as concentration quenching of the luminescence. Concentration quenching occurs as a result of a very efficient energy transfer process between the luminescent centers; it starts to have significant effect at a concentration for which there is a considerable reduction in the mean distance between the interacting centers. Two mechanisms are generally invoked to explain the concentration quenching: energy transfer between the lanthanide ions and defects of the host, and interactions between the lanthanide ions. In the first case due to a very efficient energy transfer, excitation energy migrates to a large number of centers being finally transferred to lattice defects or impurity ions that act as energy acceptors. These acceptors can relax to their ground state by multi-phonon emission or light emission at wavelengths different from those characteristic of the lanthanides. These kinds of energy acceptor centers are called *killer* or *quenching traps*, and acts as energy sink within the chain transfer, thus quenching the luminescence of the lanthanide ions. The second type of mechanisms is due to energy dissipation via cross relaxation by means of resonant energy transfer between two identical adjacent centers. At large concentrations new kind of centers can be formed, due to clustering of the individual ions. This leads to rearrangements of the energy levels that can strongly affect the fluorescence properties [13]. Thus the emission spectra were observed for excitation wavelength of 254 nm. The maximum emission intensity was observed for 1 m % concentration of Mn doped sample [Fig. 4]. The emission intensity was almost reduced to half for the samples containing 0.5 m %, 2 m % and 5 m % of Mn doping concentration. Thus at emission side also concentration quenching effect was observed. It is thereby concluded that in  $Ca_2B_2O_5$  host the effect of concentration quenching is observed. The emission intensity decreases below and above the critical dopant concentration of 1 m %.

#### IV. CONCLUSION

Calcium borate phosphor  $Ca_2B_2O_5:Mn^{2+}$  converts the ultraviolet radiation of mercury discharge of UV-C range (254 nm) into longer wavelength range UV-A (315-380 nm). Such converted UV-light is applicable in medicine for phototherapy of skin diseases (in particular, psoriasis), in cosmetics for artificial sunburn, in photocopy equipments, for photo-polymerization, UV-hardening, metal defectoscopy, for checking up banknotes, for creating decorative-advertising effects in illumination and many other purposes, for ultraviolet (UV) light sources, light emission diodes (LEDs), and luminescent phosphors.  $Ca_2B_2O_5:Mn^{2+}$  was prepared by single step combustion synthesis for different  $Mn^{2+}$  concentrations and its crystal structure and effect of concentration quenching for photoluminescence emission spectra were observed.

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