Combustion synthesis and optical properties of Oxy-borate phosphors YCa₄O(BO₃)₃:RE³⁺ (RE = Eu³⁺, Tb³⁺) under UV, VUV excitation

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A B S T R A C T
The inorganic oxy-borate host phosphors YCa₄O(BO₃)₃:RE³⁺ (RE = Eu³⁺, Tb³⁺) were synthesized by a novel solution combustion technique. The synthesis is based on the exothermic reaction between the fuel (Urea) and oxidizer (Ammonium nitrate). The heat generated in reaction is use for auto combustion of precursors. The structures of the prepared samples were confirmed by powder XRD technique. The photoluminescence properties of the powder samples were investigated under UV and VUV excitation; “The phosphor YCa₄O(BO₃)₃:Eu³⁺ and YCa₄O(BO₃)₃:Tb³⁺ shows strong absorption in UV and VUV region and exhibits intense red and green emission upon excited by 254 nm UV and 147 nm VUV Radiation”.

1. Introduction

Rare earth borates and oxyborates have been widely investigated as host materials for phosphors. Borates and oxyborate materials possess unique properties high ultraviolet transparency, exceptional optical damage threshold, wide band gap and high stability which makes them attractive for numerous practical applications [1–6]. Most of the rare earth borates are optically transparent up to 140–180 nm, so that the VUV light can directly excite impurity activator in these hosts [7]. The strong absorption due to the impurity ions would give efficient conversion of the VUV light. Phosphors in the PDP are excited by vacuum-ultraviolet (VUV) radiation lines of Xe atoms at 147 nm and Xe light. Phosphors in the PDP are excited by vacuum-ultraviolet (VUV) radiation lines of Xe atoms at 147 nm and Xe light. The inorganic oxy-borate host crystals excited by the VUV light to the Eu³⁺ and the Tb³⁺ have attracted attention as red emitting phosphors for plasma display panels (PDPs) [4–6]. The absorption band of the borate host lattice and the charge transfer state (CTS) transition of Eu³⁺ in these compounds are located in the VUV and the UV regions, respectively. The energy transfer from a borate host crystal excited by the VUV light to the Eu³⁺ activator leads to host-excited luminescence [8–10]. At present the most widely used green-emitting phosphor for PDP is Zn₅SiO₄:Mn²⁺ (ZSM). Although it is a good phosphor widely used in plasma display panels but, the decay time is too long for color TV application [11,12]. Thus special attention has paid to improve shorter decay time as green emission of Tb³⁺ ion (7D₄ → 5Fₓ) is expected to have a relatively short decay time. Some phosphors such as Y₃Al₅O₁₂:Tb, Ln₅Al₅O₁₇:RE (Ln = Y, Gd; RE = Eu, Tb), Y₀.₃₅Gd₀.₆₅BO₃ and Sr₃(PO₄)₂:Tb [13,14] have been reported. YCa₄O(BO₃)₃ doped with Eu,Tb synthesized by conventional method was reported by Tian et al. [15]. As a progressive research, in the present work, one of the oxyborates, YCa₄O(BO₃)₃ prepared by a novel combustion method and doped with Eu³⁺ and the Tb³⁺ have been investigated as a host material for PDP phosphor applications. The crystal structure of calcium–rare earth oxyborates with the composition RECa₄O(BO₃)₃ (RE = Y,Gd,La) have been reported by Norrestam et al. [16]. The oxyborates, YCa₄O(BO₃)₃ doped with Eu³⁺ and the Tb³⁺ exhibits efficient emission under UV and VUV excitation. The 4f⁵5d state of Tb³⁺ and the charge transfer state of Eu³⁺ are observed as strong excitation bands in the UV, VUV region. Both of these processes are allowed optical transitions [16–18].

2. Experimental

2.1. Combustion synthesis of YCa₄O(BO₃)₃:RE³⁺ (RE = Eu³⁺, Tb³⁺)

The samples were prepared by a novel solution combustion technique [19–24]. The starting ingredients Y(NO₃)₃, Eu(NO₃)₃ and Tb(NO₃)₃ (IRE Ltd.), Ca(NO₃)₂, H₃BO₃, NH₄NO₃ and NH₃–CO–NH₃ (5 D Fine AR) were used. The stoichiometric amounts of the ingredients were thoroughly mixed in an Agate Mortar, adding little amount of double distilled water and obtained an aqueous homogeneous solution.

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The aqueous solution was then transferred into a china basin and introduced into a preheated muffle furnace maintained at 550 °C. The solution boils, foams and ignites to burn with flame and obtained a voluminous, foamy powder. The entire combustion process was over in about 5 min following the combustion, the resulting fine powders were annealed in a slightly reducing atmosphere provided by burning charcoal at temperature 900 °C for about 90 min. and suddenly cooled to room temperature. The stoichiometric amount of precursors required is obtained using coefficients in balanced chemical reaction (Table 1).

### Table 1

<table>
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<tr>
<th>S.N.</th>
<th>Product Corresponding reaction with balanced molar ratios of precursors</th>
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<tr>
<td>1.</td>
<td>YCa₄(O(BO₃))₃:Eu³⁺ 0.95Y(NO₃)₃ + 4Ca(NO₃)₂ + 3H₃BO₃ + 10CO(NH₂)₂ + 2.5 NH₄NO₃ + 0.05 Eu(NO₃)₃ → YCa₄(O(BO₃))₃:Eu³⁺ + Gaseous products (H₂O, NH₃ and NO₂)</td>
</tr>
<tr>
<td>2.</td>
<td>YCa₄(O(BO₃))₃:Tb³⁺ 0.97Y(NO₃)₃ + 4Ca(NO₃)₂ + 3H₃BO₃ + 10CO(NH₂)₂ + 2.5 NH₄NO₃ + 0.03 Tb(NO₃)₃ → YCa₄(O(BO₃))₃:Tb³⁺ + Gaseous products (H₂O, NH₃ and NO₂)</td>
</tr>
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2.2. Characterization of samples

The X-ray diffraction (XRD) pattern of host sample of YCa₄O(BO₃)₃ was recorded on Rigaku MiniFlex diffractometer with scan speed 2000 deg/min. The morphology of the phosphor particles was studied by using Hitachi model S-4800 field emission scanning electron microscope and elemental analysis by Bruker EDS. UV PL and PLE measurements at room temperature were performed on a Hitachi F-7000 spectrophotometer equipped with a 450 W Xenon lamp in the range 200–600 nm, with spectral slit width of 2.5 nm. VUV PL spectra were measured by FL5-020T fluorescence spectrophotometer with a VM-504-type vacuum monochromator using a deuterium lamp as the lighting source. The excitation spectrum can be corrected by sodium salicylate, whose quantum efficiency is almost constant in this region. All the measurements were performed at room temperature. The region of excitation spectra was from 100 nm to 300 nm and the emission spectra recorded under 147 nm excitation.

2.3. XRD analysis

The powder X-ray diffraction (XRD) profile of synthesized YCa₄O(BO₃)₃:RE (RE = Eu³⁺, Tb³⁺) is shown in Fig. 1. It is in good agreement with ICDD card No. 00-050-0403 of host lattice of YCa₄O(BO₃)₃. The space group is monoclinic Cm and the rare-earth ion site has Cs symmetry in a distorted octahedral coordination with cell parameters a = 8.078 Å, b = 16.022 Å and c = 3.534 Å and interfacial angles α = γ = 90° and β = 101.19°. Four oxygen ions belong to the borate groups, and the other two are free oxygen ions. "The free oxygen ions are not bound to boron and are coordinated in a way similar to that in the simple rare earth compounds, and the rare earth ions are having well defined rosette morphology and some agglomerations are observed."

### 2.4. Surface morphology

The FE-SEM micrographs of YCa₄O(BO₃)₃:Eu³⁺ and YCa₄O(BO₃)₃:Tb³⁺ prepared under the same conditions are shown in Fig. 2. The SEM images shows that particles are having well defined rosette morphology and some agglomerations are observed. The average size of particles is about 1–2 μm suitable for high energy VUV absorption and emission from exterior surface of phosphor particles. "EDS photographs in Fig. 3 shows that the rare-earth elements have been included into the phosphors."
The UV PL spectra of YCa₄O(BO₃)₃:Tb³⁺ is depicted in Fig. 6. The UV excitation spectrum shows an intense broad band in the wavelength range from 210 nm to 250 nm with a maximum at 240 nm. The strong excitation band is due to the spin-allowed 4f⁸ → 4f⁹5d transition (ΔS = 0) of Tb³⁺ ion. The emission spectrum for 254 nm excitation shows intense Green line at 547 nm, corresponding to the 5D⁴ → 7F₅ transition. The VUV emission spectra of YCa₄O(BO₃)₃:Tb³⁺ (3%) under 147 nm excitation is shown in Fig. 7. The major emission peaks of Tb³⁺ originates from 5D₃ → 7F₅ (J = 3, 4, 5, 6) and the emission from higher level 5D₄ is very weak. In borate hosts, the relative intensity of the 5D₃ emission is much weaker than it is in other host materials like phosphate, silicates, and aluminates [15]. Among the emission lines from the 5D₃ state, the dominant emission is observed at 547 nm, corresponding to the 5D₄ → 7F₅ transition. The most prominent emission, 5D₄ → 7F₅ peaking at 547 nm, results in a green color with excellent purity and with a CIE chromaticity coordinate of (0.28, 0.70) [25]. Chromatic point is shown in Fig. 8.
4. Conclusion

The inorganic Oxy-borate host phosphor YCa$_4$O(BO$_3$)$_3$:RE (RE = Eu$^{3+}$, Tb$^{3+}$) was prepared by a solution combustion technique. The combustion synthesis is simple, time saving, low temperature and inexpensive novel technique. Powder XRD pattern confirmed the formation desired product. Under 254 nm UV excitation and 147 nm VUV excitation YCa$_4$O(BO$_3$)$_3$:Eu$^{3+}$ exhibits strong absorption and efficient emission in the red region of the spectrum, under identical condition YCa$_4$O(BO$_3$)$_3$:Tb$^{3+}$ shows prominent emission line occurs at 547 nm in intense green region. These phosphors could be potential candidates for PDP applications.

References