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ORIGINAL ARTICLE

Investigation of Boron-doping Effect on Photoluminescence Properties of $CdNb_2O_6$: Eu^{3+} Phosphors

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Abstract Pure, Eu^{3+} − doped and Eu^{3+},B^{3+} co-doped $CdNb_2O_6$ powders have been prepared by a molten salt synthesis method using Li_2SO_4/Na_2SO_4 salt mixture as a flux at a relatively low temperatures as compared to solid state reaction. X-ray diffraction patterns of pure $CdNb_2O_6$ samples indicated orthorhombic single phase. Photoluminescence investigations of $CdNb_2O_6$ samples showed a strong blue emission band centered at 460 nm. For Eu-doped $CdNb_2O_6$ samples, the luminescence of Eu^{3+} was observed with the host red emission varying with the Eu-doping concentrations. This PL characteristic of the doped samples may be attributed to the energy transfer between Eu^{3+} and niobate groups (NbO_6). Boron incorporation has remarkably increased the luminescence of Eu^{3+}-doped $CdNb_2O_6$.

Keywords Molten salt process · Luminescence · Columbite cadmium niobate · Boron effect

Introduction

Niobates are known as interesting photoactive host materials, and the luminescent properties of perovskite and columbite-type niobates activated with and without rare earth ions have been studied previously [1–4]. The luminescence properties of metal niobates with columbite structure were investigated by Watchel in 1960's [5]. However, a few investigations exist on the $CdNb_2O_6$ columbite metal niobates.

The $CdNb_2O_6$ has an ordered columbite structure where the pentavalent cations form pairs by face sharing of their coordination octahedral. $CdNb_2O_6$ is an essential intermediate phase for the synthesis of $Cd_2Nb_2O_7$ ferroelectric ceramics [6] and it is also a good reference material for some dielectric ceramics [7]. Cadmium niobates take attention as microwave dielectric resonators [8]. Cadmium niobate exhibits a broad and bright blue emission peaks at about 460 nm with the excitation by UV radiation at 272 nm at room temperature [9].

The molten salt process is a low-temperature process, and gives better chemical homogeneity and finer particles together with better control of particle morphology than those produced by the mixed oxide route. These features make the molten salt process a promising method since it results in improved sinterability [10].

Incorporation of the flux to promote the sintering reaction is a well-known route to expedite the sintering and/or crystal growth reaction. Boron compounds are widely used as the flux for the conventional solid-state reaction because of its low melting point.

Boron oxide (B_2O_3) having the melting point of 460 °C is the most used boron compound for the flux. Boron oxide has been also used as a co-dopant with rare earth ions such as Eu^{3+} [11].

Boric acid dehydrates to meta boric acid in the first step and then melts by converting to boron tri oxide (B_2O_3) at 460 °C according to this reaction ($H_3BO_3 \rightarrow HBO_2 + H_2O$, $2HBO_2 \rightarrow B_2O_3 + H_2O$). Because of the vapor pressure of the boron tri oxide is quite high (1.16×10^{-6} Pa) at 460 °C, İt's a well-known fact that the B_2O_3 has highly volatility. Hence, depending on the evaporation, boron deficiency may be

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occurred during the calcination process. To prevent this, excessive amount of boron should be added into the reaction [12].

We have believed in our study that, selected boron molar rates were indisputably much to prevent lack of boron, because we have achieved to synthesize the single-phase co-doped samples for each reaction. The reason for the formation of the 5, 15, 25 mol% B^{3+} co-doped single phase powders without any boron evaporation can be explained by the homogene dispersion of the reactants and the dopants in Li_2SO_4-Na_2SO_4 flux and most likely, incorporation of boron into the columbite lattice structure due to its lower ionic radii (0.27 Å) [13].

To our knowledge, only a few papers pertaining to the structural and luminescence properties of the Eu^{3+} doped $CdNb_2O_6$ have been observed in the literature [14, 15] however there is readily no publication has been reported on the synthesis of Eu^{3+} and B^{3+} co-doped $CdNb_2O_6$ powders and effect of boron on the luminescence characteristics of the $CdNb_2O_6$ host and Eu^{3+} ions.

In this study, $CdNb_2O_6$: (Eu^{3+},B^{3+}) activated single phase phosphor powders were achieved by the molten salt synthesis method and the structural analysis, phase morphology and the luminescence behavior of both Eu^{3+} doped and Eu^{3+},B^{3+} co-doped single phase powders described and discussed in detailed.

Materials and Methods

Undoped and Eu^{3+}-doped $CdNb_2O_6$ powders were prepared by the molten salt synthesis method by using cadmium nitrate [$Cd(NO_3)_2{\cdot}4H_2O$] (Aldrich, 98.5 %), niobium oxide (Nb_2O_5) (Sigma, 99.9 %), europium oxide (Eu_2O_3) (Aldrich, 99.9 %) as a rare earth (RE) dopant and boric acid (H_3BO_3) as a co-dopant. Li_2SO_4:Na_2SO_4 at a molar ratio of 0.635:0.365 having melting temperature of 594 °C was used as a salt mixture. The weight ratio (W) of salts/oxides was 1:1. The stoichiometric amount of cadmium nitrate, and niobium penta oxide were weighted out and mixed in an agate mortar to obtain a homogeneous mixture. On the other hand, lithium sulphate-sodium sulphate binary salt mixtures in a stoichiometric amount were mixed in another porcelain mortar. Both oxides and molten salt mixtures were mixed homogeneously in an agate mortar at a weight ratio of 1:1.

In the molten salt synthesis of $CdNb_2O_6$, different salt/oxide molar ratios and calcination temperatures were used to determine the optimum molar ratio and synthesis temperature to produce single phase columbite cadmium niobate. Synthesis parameters of the $CdNb_2O_6$ powders were also given in Table 1.

A sufficient amount of mixtures was put into alumina crucible and then heat treated for 4 h at different temperatures. After that, calcined products were washed several times with hot distilled ultra-pure water to purify the oxides by eliminating the salts. Then, they vacuum filtered several times, until not to observe any amounts of turbidity caused by the ions which sourced from different salts in the filtered water. To determine the SO_4^{2-} ions in filtered water by qualitative analysis, 1 M $Ba(NO_3)_2$ solution was used and purified samples were dried at 110 °C.

The similar synthesis procedure used for Eu^{3+}-doped $CdNb_2O_6$ and the doping concentration of Eu^{3+} was varied as 0.5, 3.0 and 6.0 mol%.

The synthesis procedure of Eu^{3+},B^{3+} co-doped $CdNb_2O_6$ has been synthesized in same manner, except that B_2O_3 was introduced into the reaction media as a co-dopant in the molar ratios of 5, 15, 25 % respectively.

Table 1 Synthesis parameters of $CdNb_2O_6$ powders and their phase compositions

Compound	Salt System and Salt/Salt Molar Ratio	Salt/Oxide WeightRatio	Heat Treatment	Phases
$CdNb_2O_6$	Li_2SO_4/Na_2SO_4 0.635/0.365	1:1	630 °C, 4 h	$CdNb_2O_6$
$CdNb_2O_6$	Li_2SO_4/Na_2SO_4 0.635/0.365	1:1	700 °C, 4 h	$CdNb_2O_6$
$CdNb_2O_6$	Li_2SO_4/Na_2SO_4 0.635/0.365	1:1	800 °C, 4 h	$CdNb_2O_6$
$CdNb_2O_6$	Li_2SO_4/Na_2SO_4 0.635/0.365	1:1	900 °C, 4 h	$CdNb_2O_6$
0.5 mol% Eu^{3+} doped $CdNb_2O_6$	Li_2SO_4/Na_2SO_4 0.635/0.365	1:1	900 °C, 4 h	$CdNb_2O_6$
3.0%mol Eu^{3+} doped $CdNb_2O_6$	Li_2SO_4/Na_2SO_4 0.635/0.365	1:1	900 °C, 4 h	$CdNb_2O_6$, $Cd_2Nb_2O_7$
6.0%mol Eu^{3+} doped $CdNb_2O_6$	Li_2SO_4/Na_2SO_4 0.635/0.365	1:1	900 °C, 4 h	$CdNb_2O_6$, $Cd_2Nb_2O_7$

The phases formed in the samples after heat treatment and the crystal structure were determined by X-ray diffraction (XRD) using a Rigaku D-Max 2200 X-ray diffractometer system with graphite monochromatized Cu Kα irradiation (λ = 1.5418 Å). The morphology and size of the powders were detected using a JEOL JSM 5910 LV scanning electron microscope (SEM). Excitation and emission spectra of doped and undoped ceramics were measured with a Scinco Floromaster FS/2 model fluorescence spectrophotometer at room temperature.

Results and Discussion

X-Ray Diffraction (XRD) Results

The XRD patterns of pure $CdNb_2O_6$ powders prepared at different temperatures between 630 ~ 900 °C for 4 h are shown in Fig. 1.

The XRD revealed only single phase $CdNb_2O_6$ with columbite structure (JCPDS No =38–1428) and no secondary phases were detected. Although an intermediate phase ($Cd_2Nb_2O_7$; JCPDS No =18–0258) formation was reported by the other researchers [16] at 700 °C, it was eliminated by using molten salt synthesis even at 630 °C. The elimination of intermediate phase by molten salt synthesis can be explained by the homogenizing of the powders which enhanced the diffusion process. However, the crystallinity of the powders increased with increasing the heat treatment temperature and no other inter phases have been observed in the pure powders.

Figure 2 shows the XRD patterns of 0.5, 3.0 and 6.0 mol% Eu^{3+}-doped $CdNb_2O_6$ powders annealed at 900 °C. Although single columbite cadmium niobate structure was obtained for 0.5 mol% Eu-doped $CdNb_2O_6$, the second phase, $Cd_2Nb_2O_7$ (JCPDS Card No =34–0404), started to form at 3.0 mol% Eu^{3+} doping and its peak intensity increased with increasing dopant concentration.

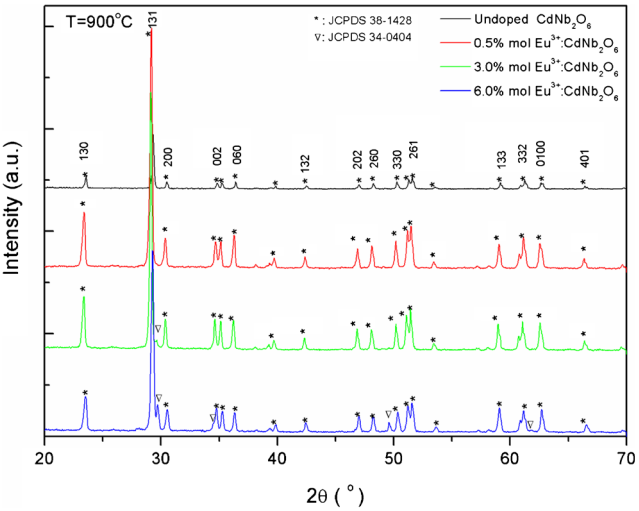

Fig. 2 X-ray diffraction patterns of $CdNb_2O_6$ powders doped with **a** 0.5, **b** 3, and **c** 6 mol% Eu^{3+} annealed at 900 °C for 4 h

According to the XRD analysis results of the both 0.5 and 6 mol% Eu^{3+} and 5, 15, 25 mol% B^{3+} co-doped $CdNb_2O_6$ powders respectively, orthorhombic single-phase has been determined for all synthesis without any other interphase formation which showed as Fig. 3.

In that regard, 0.5 and 6 mol% europium and 5, 15, 25 mol% boron co-dopants have good dissolved in the $CdNb_2O_6$ host structure. For this reason, when consider the ionic ratio of Eu^{3+} (1.08 Å), B^{3+} (0.27 Å) and Cd^{2+} (0.95 Å) ions, they are capable to form concomitant solid melt in the host structure and Eu^{3+} and B^{3+} ions may cause a

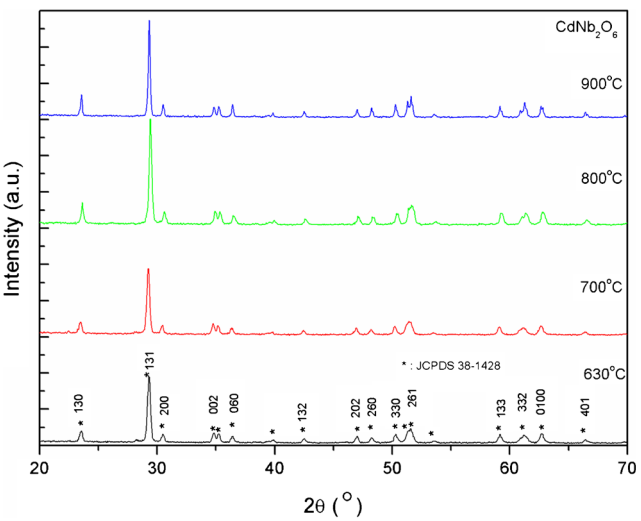

Fig. 1 X-ray diffraction patterns of pure $CdNb_2O_6$ powders annealed at **a** 630 °C, **b** 700 °C, **c** 800 °C, **d** 900 °C for 4 h

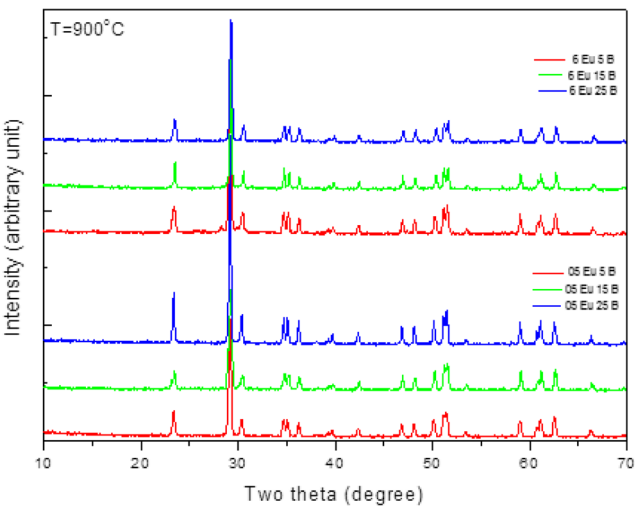

Fig. 3 XRD patterns of 0.5 and 6 mol% Europium and 5, 15, 25 mol% boron co-doped powders

change on the charge density of the oxygen coordination in CdO_6 octahedral is considered.

Scanning Electron Microscopy (SEM) Results

The pure, 0.5 and 6.0 mol% Eu^{3+} − doped $CdNb_2O_6$ powders calcined at 900 °C shown in Fig. 3a–c have irregular, agglomerated, and plate-like shapes. The average particle sizes of three powders annealed at 900 °C were about 2.9–4.0 μm. The corresponding SEM and XRD results confirm each other. While one structure was observed for a single phase in both powders of pure and 0.5 mol% Eu^{3+} doped $CdNb_2O_6$, two different structures were observed for two phases in 6.0 mol% Eu^{3+} − doped $CdNb_2O_6$ (Fig. 4).

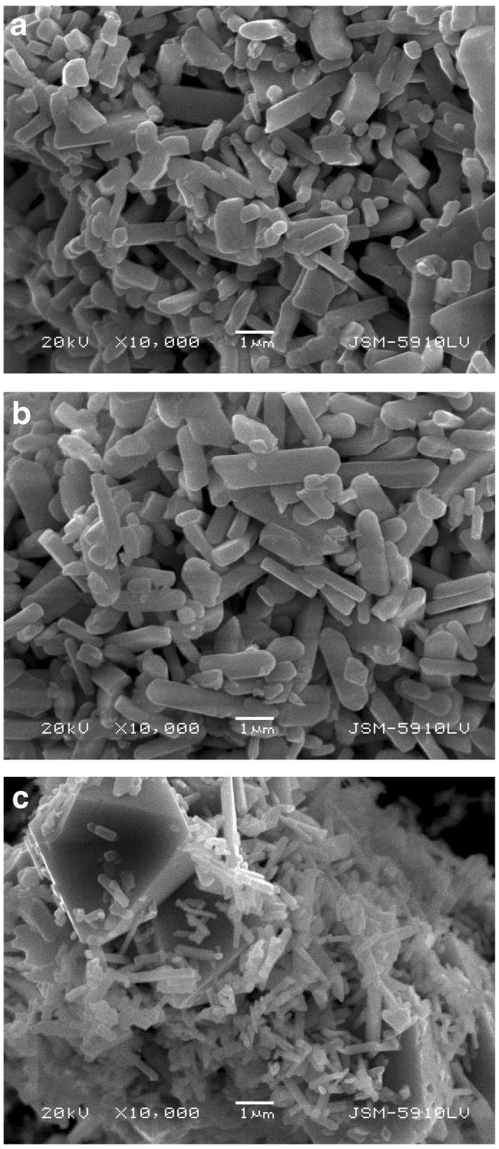

Fig. 4 **a–c** The SEM micrographs of the pure, 0.5 and, 6.0 mol% Eu^{3+}-doped $CdNb_2O_6$ powders calcined at 900 °C for 4 h

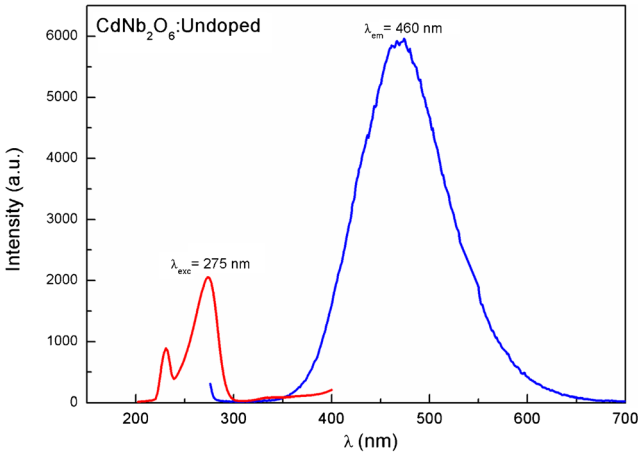

Fig. 5 The PL emission spectral wavelength curves of pure $CdNb_2O_6$ powder under 275 nm UV excitation at room temperature

Spectrofluorometric Results in UV-Vis Spectral Region

Blasse [17] reported that the columbite niobate compounds had two typical energy absorbing octahedral groups as $[NbO_6]^{7-}$ and $[NbO_4]^{3-}$, respectively. Consequently, absorption of the excitation energy leads two characteristic excitation bands which are associated with the direct excitation of the $CdNb_2O_6$ host, via the charge transfer transition between Nb and O atoms. The peak of excitation, at about 272 nm, can be associated with charge transfer bands of $[NbO_6]^{7-}$ in the $CdNb_2O_6$ system [18, 19].

The PL emission spectral wavelength curves of pure $CdNb_2O_6$ powder under 275 nm UV excitation at room temperature are shown in Fig.5.

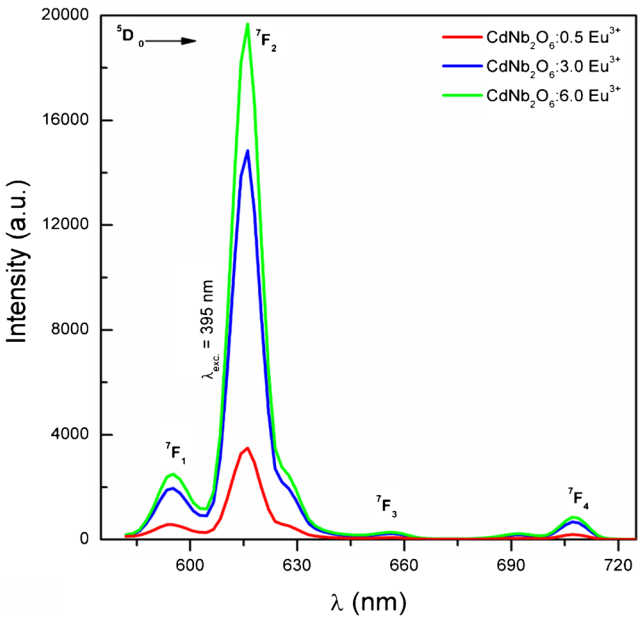

Fig. 6 The room temperature excitation, and emission spectra of $CdNb_2O_6$ doped with 0.5, 3 and 6 mol% Eu^{3+}

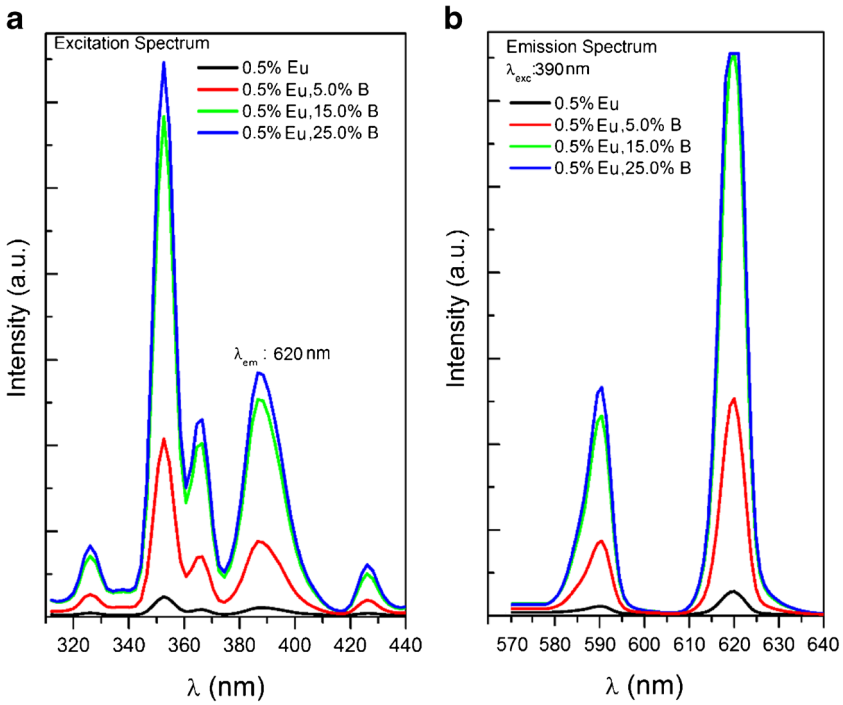

Fig. 7 The room-temperature **a** excitation $_{em}$ = 620 nm) spectra, and **b** emission $_{ex}$ = 390 nm) spectra of 0.5 mol% Eu^{3+} and 5, 15, 25 mol% B^{3+} co-doped $CdNb_2O_6$ powders

The photoluminescence (PL) spectra shows a broad and strong blue emission peak at about 460 nm. In columbite structure, the edge-shared NbO_6 groups are efficient luminescent centers for the blue emission, which may be attributed to self-trapped exciton recombination [20]. In other words, this luminescence was originated from the crystals of absorbing groups of the niobate octahedral group $[NbO_6]^{7-}$ as stated above.

The PL emission spectral wavelength curves of 0.5, 3.0, 6.0 mol% Eu^{3+}-doped $CdNb_2O_6$ powders under 395 nm excitation at room temperature are shown in Fig. 6.

When a rare earth ion invades a centrosymmetric site in host matrix, optical transitions between the $4f^n$ configurations are forbidden in terms of electric dipole transition. If there is no inversion symmetry at the site of dopant in the host lattice (non-centrosymmetric site), electric dipole transitions may occur between $^5D_0 \rightarrow {}^7F_2$ energy levels. Generally, if Eu^{3+} dopants locate on the non-centrosymmetric crystallographic sites in host lattice, a red emission resulted from $^5D_0 \rightarrow {}^7F_2$ (615 nm) electric dipole transition, while orange emission caused from $^5D_0 \rightarrow {}^7F_1$ (590 nm) magnetic dipole transition [21].

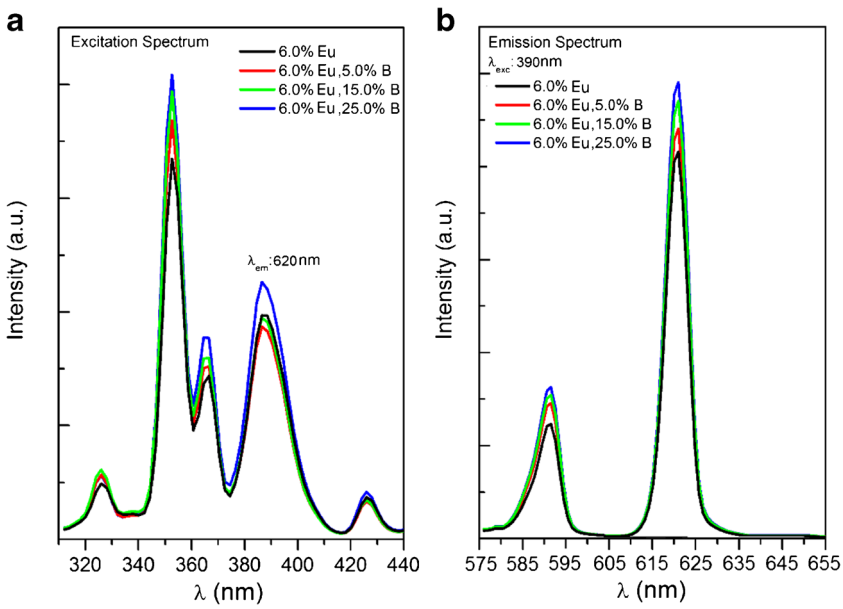

Fig. 8 The room-temperature **a** excitation $_{em}$ = 620 nm) spectra, and **b** emission $_{ex}$ = 390 nm) spectra of 6 mol% Eu^{3+} and 5, 15, 25 mol% B^{3+} co-doped $CdNb_2O_6$ powders

As it's seen from the PL spectra of Eu^{3+} doped $CdNb_2O_6$ powders, $^5D_0 \rightarrow {}^7F_2$ electric dipole transition around 615 nm is stronger than the magnetic dipole transition around 590 nm.

Thus, a predominant red emission was observed at 615 nm. By increasing the Eu^{3+} doping concentration, much more Eu^{3+} ion was entered into the non-centrosymmetric sites in the $CdNb_2O_6$ columbite structure and so, emission intensity increased.

As illustrated at Fig. 7, by increasing of boron doping concentration, emission intensity of 0.5 mol% Eu^{3+} doped $CdNb_2O_6$ increased. This might be attributed to the energy transfer from B^{3+} to Eu^{3+}. Two main factors can be estimated for enhancing the luminescence intensity; (i) change in the oxygen coordination symmetry surrounding the Eu^{3+} ions, (ii) the presence of ions like $Eu^{3+}$and B^{3+} that have relatively smaller ionic radii and their effect on crystal field strength of the oxygen coordination in $CdNb_2O_6$ lattice structure.

Figures 7 and 8 show that, by excitation of the 0.5 and 6 mol% Eu^{3+} and 5, 15, 25 mol% B^{3+} co-doped $CdNb_2O_6$ powders at 390 nm, exhibited two characteristic emission peaks at 590 nm and 620 nm as expected. However, incorporation of 5, 15, 25 mol% B^{3+} ion into the host lattice, remarkably increased the emission intensity of B^{3+} doped sample when compare to 0.5 mol% Eu^{3+} doped samples that without boron doping.

Conclusion

This work has shown that, pure $CdNb_2O_6$ crystal was successfully prepared by molten salt synthesis method at 630–900 °C without any minor phase formation. $CdNb_2O_6$: (Eu^{3+}, B^{3+}) co-doped phosphors were also successfully obtained by molten salt synthesis method. While a single phase observed in both powders of pure and 0.5 mol% Eu^{3+} doped $CdNb_2O_6$, two different phases were observed for 3.0 mol% and 6.0 mol% Eu^{3+} doped $CdNb_2O_6$. By excitation of the 0.5, 3.0 and 6.0 mol% Eu^{3+} doped $CdNb_2O_6$ powders at 395 nm, they have exhibited two characteristic band pass emissions at 590 and 615 nm respectively. The photoluminescence results of the all doped samples show that the photoluminescence increased as the dopant concentration increase without any concentration quenching due to energy transfer between excessive neighbor Eu^{3+} ions. It has revealed that, boron ion is a very good co-activator in terms of its excellent luminescence increasing activity with high melting properties without any secondary phase formation. The strongest emission band of the Eu^{3+} doped $CdNb_2O_6$ sample peaks at about 615 nm may be a good candidate for the use of the present material as a red phosphor for lighting devices. Therefore, it appears justified concluding that orthorhombic columbite $CdNb_2O_6$ activated with Eu^{3+} ions can be considered as an interesting and promising luminescent and multifunctional material.

The present study also showed that divalent cadmium ions can be substituted by trivalent lanthanide ions and accompanied another trivalent ion like boron as a co-dopant in crystalline columbite niobates.

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