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Synthesis, characterization and photoluminescence properties of Eu^{3+} doped columbite $CdNb_2O_6$

Mete Kaan Ekmekçi[a,*], Murat Erdem[b], Mustafa Ilhan[c], Ali Sadi Başak[a], Ayhan Mergen[c]

[a] Marmara University, Department of Chemistry, Kadıkoy 34777, Istanbul, Turkey
[b] Marmara University, Department of Physics, Kadıkoy 34777, Istanbul, Turkey
[c] Marmara University, Department of Material and Metallurgy Eng., Kadıkoy 34777, Istanbul, Turkey

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ABSTRACT

Pure and Eu^{3+}-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 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).

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1. 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 1960s [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]. The 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 [8].

The molten salt process is a low-temperature process, and gives better chemical homogenity 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 [9].

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 [10,11]. In the present work, the phase formation, morphology and photoluminescence (PL) characteristics of $CdNb_2O_6$: Eu^{3+} powders firstly synthesized by molten salt route have been studied in detail and discussed.

2. 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. 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 pentaoxide 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

* Corresponding author. Tel.: +90 216 345 1242; fax: +90 216 347 87 83.
E-mail address: mekmekci@marmara.edu.tr (M.K. Ekmekçi).

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

Compound	Salt system and salt/salt molar ratio	Salt/oxide weight ratio	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	$CdNb_2O_6$, $Cd_2Nb_2O_7$

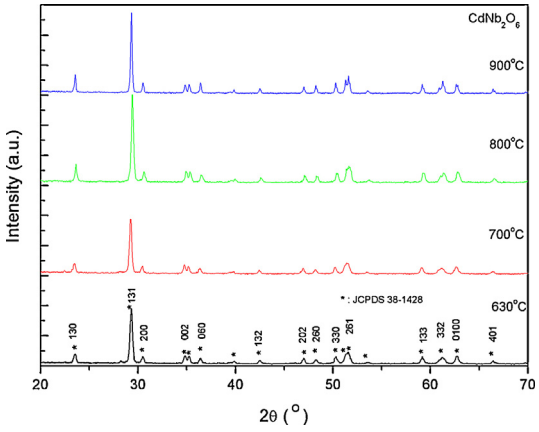

Fig. 1. X-ray diffraction patterns of pure $CdNb_2O_6$ powders annealed at (a) 630 °C, (b) 700 °C, (c) 800 °C and (d) 900 °C for 4 h.

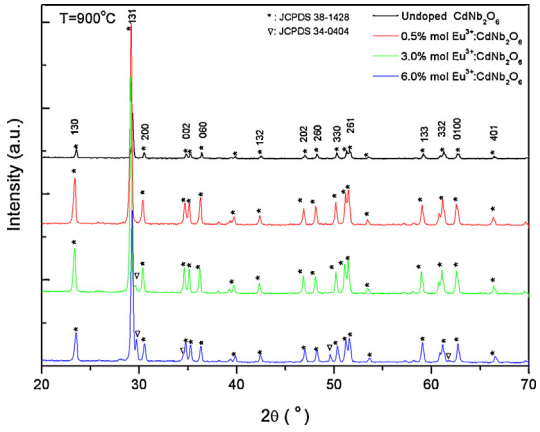

Fig. 2. X-ray diffraction patterns of $CdNb_2O_6$ powders doped with (a) 0.5, (b) 3 and (c) 6 mol% Eu^{3+} annealed at 900 °C for 4 h.

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 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.

3. Results and discussion

3.1. X-ray diffraction (XRD) results

The XRD patterns of pure $CdNb_2O_6$ powders prepared at different temperatures between 630 and 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 [12] 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.

Fig. 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.

3.2. 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. 3(a–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 $CdNb_2O_6$.

3.3. Spectrofluorometric results in UV–vis spectral region

Blasse [13] 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

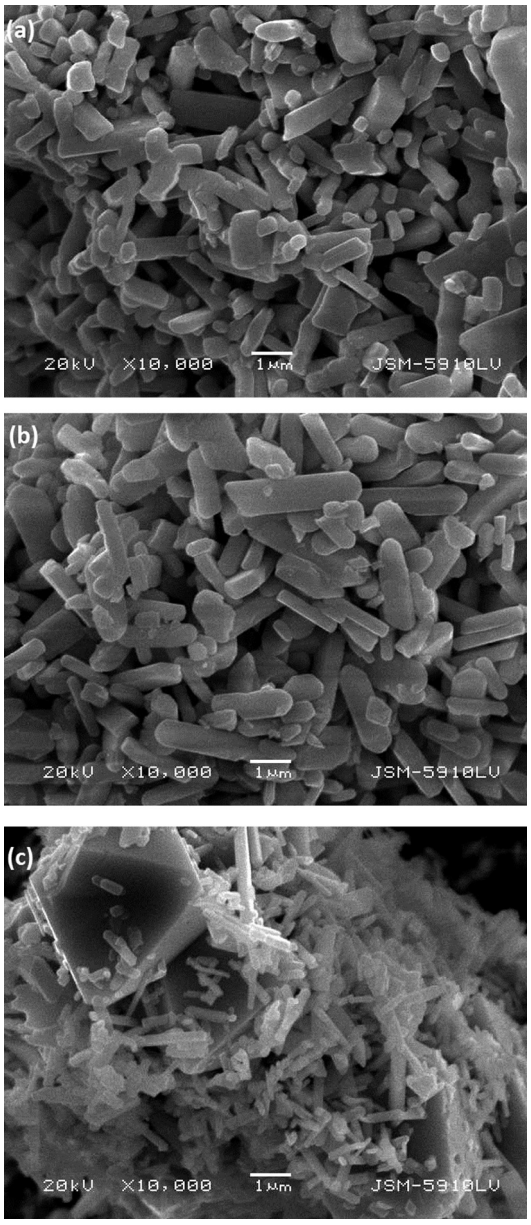

Fig. 3. (a–c) The SEM micrographs of the pure, 0.5 and, 6.0 mol% Eu^{3+}-doped $CdNb_2O_6$ powders calcined at 900 °C for 4 h.

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 [14,15].

The PL emission spectral wavelength curves of pure $CdNb_2O_6$ powder under 275 nm UV excitation at room temperature are shown in Fig. 4.

The photoluminescence (PL) spectra show 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 [16]. 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. 5.

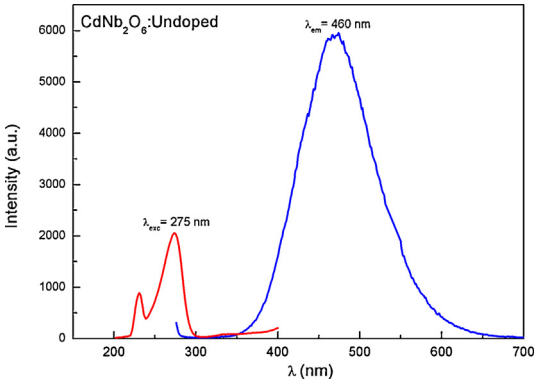

Fig. 4. The PL emission spectral wavelength curves of pure $CdNb_2O_6$ powder under 275 nm UV excitation at room temperature.

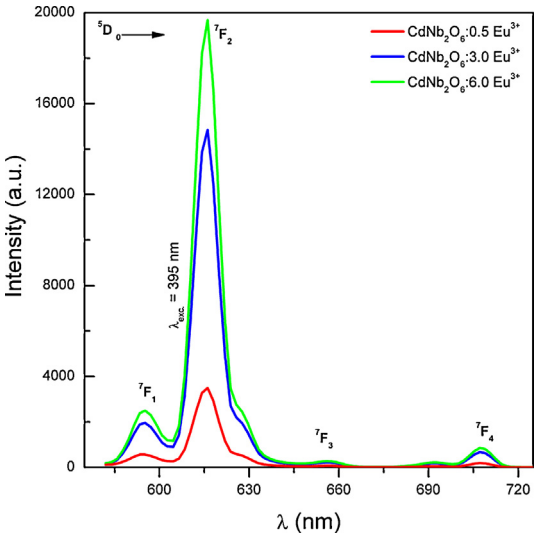

Fig. 5. The room temperature excitation, and emission spectra of $CdNb_2O_6$ doped with 0.5, 3 and 6 mol% Eu^{3+}.

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 [17].

As it is 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.

4. 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.

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 nm 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.

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.

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References

[1] G. Blasse, L.G.J. de Haart, Mater. Chem. Phys. 14 (1986) 481–484.
[2] D. Hreniak, A. Speghini, M. Bettinelli, W. Strek, J. Lumin. 219 (2006) 119–123.
[3] P. Boutinaud, L. Sarakha, R. Mahiou, J. Phys. – Condens. Matter 21 (2008) 025901–025907.
[4] A.A. Ballman, S.P.S. Porto, A. Yariv, J. Appl. Phys. 34 (1963) 3155–3156.
[5] A. Wachtel, J. Electrochem. Soc. 111 (1964) 534–538.
[6] C.M. Ronconi, O.L. Alves, Thin Solid Films 441 (2003) 121–129.
[7] M.K. Ekmekçi, M. Erdem, A. Mergen, G. Özen, B. Di Bartolo, J. Alloy. Compd. 591 (2014) 230–233.
[8] Y.J. Hsiao, Y.S. Chang, G.J. Chen, Y.H. Chang, J. Alloy. Compd. 471 (2009) 259–262.
[9] S. Zhao, Q. Li, L. Wang, Y. Zhang, Mater. Lett. 60 (2006) 425–430.
[10] G. Blasse, M.G.J. van Leur, Mater. Res. Bull. 20 (1985) 1037–1045.
[11] H.G. Brittaina, W.A. McAllister, Spectrochim. Acta A 41 (1985) 1041–1046.
[12] Y.J. Hsiao, T.H. Fang, S.S. Chi, Open Serv. Sci. J. 1 (2009) 30–33.
[13] G. Blasse, Structure and Bonding, Springer Verlag, Heidelberg, 1980.
[14] Y. Zhou, M. Lü, Z. Qiu, A. Zhang, Q. Ma, H. Zhang, G. Zhou, Z. Yang, J. Phys. Chem. C 111 (2007) 10190–10193.
[15] W.D. Fragoso, C. De Mello Donegá, R.L. Longo, J. Lumin. 105 (2003) 97–103.
[16] A.M. Srivastava, J.F. Ackerman, W.W. Beers, J. Solid State Chem. 134 (1997) 187–191.
[17] L. Zhou, W.C.H. Choy, J. Shi, M. Gong, H. Liang, T.I. Yuk, J. Solid State Chem. 178 (2005) 3004–3009.