Materials Research Bulletin 60 (2014) 562–565

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Concentration effect of Er^{3+} ions on structural and spectroscopic properties of $CdNb_2O_6$ phosphors

Sanaz Aian Ghafouri [a], Murat Erdem [b,*], M. Kaan Ekmekçi [c], Ayhan Mergen [d], Gönül Özen [a]

[a] İstanbul Technical University, Physics Engineering, Maslak 34469, Istanbul, Turkey
[b] Marmara University, Department of Physics, Kadikoy 34722, Istanbul, Turkey
[c] Marmara University, Department of Chemistry, Kadikoy 34722, Istanbul, Turkey
[d] Marmara University, Department of Metalurgy and Material Engineering, Kadikoy 34722, Istanbul, Turkey

ARTICLE INFO

Article history:
Received 8 November 2013
Received in revised form 11 June 2014
Accepted 30 August 2014
Available online 3 September 2014

Keywords:
Ceramics
Optical materials
Luminescence
Phosphors

ABSTRACT

This study is focused on the synthesis and characterization of $CdNb_2O_6$ compounds doped with of Er^{3+} ions. Powders were synthesized by using the molten salt method and annealed at 900 °C for 4 h. The synthesized particles were structurally characterized by using X-ray diffraction, scanning electron microscopy. A single phase of the $CdNb_2O_6$ was determined and the size of the particles was found to be affected by the presence and the concentration of Er^{3+} ions. Luminescence properties of each sample were investigated by measuring accurately the emission and excitation spectra at room temperature in the wavelength range of 200–1700 nm by exciting the Er^{3+} ions at 379 nm and 805 nm. Quenching of the luminescence in both visible and near infrared spectral regions was observed to be above 1.0 mol% Er^{3+} concentration.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

High purity, compositionally uniform, single phase and uniform particle size powders are required for high resolution and high luminous efficiency in the photonic device developments. In view of the nanotechnology, moreover, it should be pointed out that the selection of host lattices and active centers for such an optical material is important [1,2].

Metal niobates such as $LiNbO_3$, $KNbO_3$ and $LaNbO_4$ are known as interesting photonic materials [3–5]. The binary niobate ceramics, with the formula $M^{2+}Nb_2O_6$ where M^{2+} = Ca, Mg, or a transition metal (TM), have the orthorhombic columbite structure and space group Pbcn (60) [6]. The cadmium niobate ($CdNb_2O_6$) is also suitable photonic material due to its thermal and, chemical stability [7]. It exhibits a broad and bright blue emission peaking at about 460 nm with the excitation by UV radiation at 272 nm at room temperature [8].

However, to the best of our knowledge, a few papers have been devoted to the study of rare earth doped cadmium niobate in the literature [9,10] no studies were made on the Er^{3+} doped cadmium niobate materials.

In this study, we present the results of a detailed investigation of the microstructure and spectroscopic properties of the erbium (Er^{3+}) doped cadmium niobate which were successfully prepared by the molten salt technique. Luminescence and excitation spectra measurements of the samples doped with Er^{3+} ions were conducted in the wavelength-range of 200–1700 nm at room temperatures.

2. Experimental study

Er^{3+} doped $CdNb_2O_6$ ceramic powders were synthesized by the molten salt method using starting materials of cadmium nitrate [$Cd(NO_3)_2{\cdot}4H_2O$], niobium oxide [Nb_2O_5], erbium oxide [Er_2O_3], and salt systems as, Li_2SO_4–Na_2SO_4 at salt/oxide with molar ratios of 1:1 and at heat treated at 900 °C. Starting materials were weighed, mixed and ground very fine in an agate mortar and pestle. The dry mixture of the precursors in the stoichiometric composition was mixed with an equal weight of salt mixture. Then the mixture was placed in a crucible and heated in a porcelain crucible at 900 °C temperature for 4 h. After thermal treatment the sulfate were removed from the products by washing with hot deionized water until the filtrates gave no reaction with barium

* Corresponding author. Tel.: +90 216 345 1242; fax: +90 216 347 8783.
E-mail address: merdem@marmara.edu.tr (M. Erdem).

http://dx.doi.org/10.1016/j.materresbull.2014.08.061
0025-5408/© 2014 Elsevier Ltd. All rights reserved.

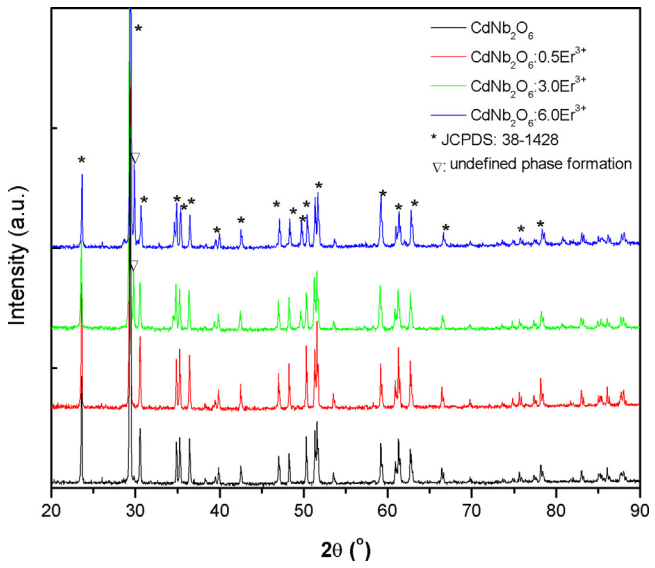

Fig. 1. The XRD pattern of $CdNb_2O_6$ powder undoped and doped with different amount of Er^{3+} synthesized with molten salt method of 900 °C for 4 h.

nitrate (1 M Ba $(NO_3)_2$) solution. Finally, the wet powders were then dried in a drying oven at 80 °C for 10 h.

X-ray Diffraction (XRD) patterns of the compounds were recorded using a Phillips PW 1800 model, equipped with a cooper X-ray tube. The measurements were taken at a generator tension of 40 kV and a current of 20 mA using CuKα rays were used to obtain the diffraction spectra from 2θ is between 10–70°, 1 °/min of scanning speed. The structural and morphological properties of the annealed powders were also investigated using scanning electron microscope (SEM, JEOL JSM 5910LV).

Room temperature diffuse reflectance spectra of the powders were obtained in the spectral range 200–1100 nm using a Perkin Elmer Model Lambda 35 UV–vis spectrophotometer to identify the absorption lines of Er^{3+} ions. Luminescence and excitation spectra of the compounds were obtained using a Scinco, Floromaster FS/2 model fluorescence spectrophotometer in the wavelength range of 200–900 nm. The luminescence spectra of the powders in the near infrared spectral region were measured using a diode laser (Apollo Instruments-S30-808-6) with the wavelength of 805.2 nm to excite the powders from the ground state ($^4I_{15/2}$) to the higher $^4I_{9/2}$ excited state of Er^{3+} ions. The luminescence from the powders was focused onto a Monochromator (Spectra SP-2-500i Model 2051) and detected by a InGaAs (ID-441-C model) detector. All the measurements were carried out at room temperature.

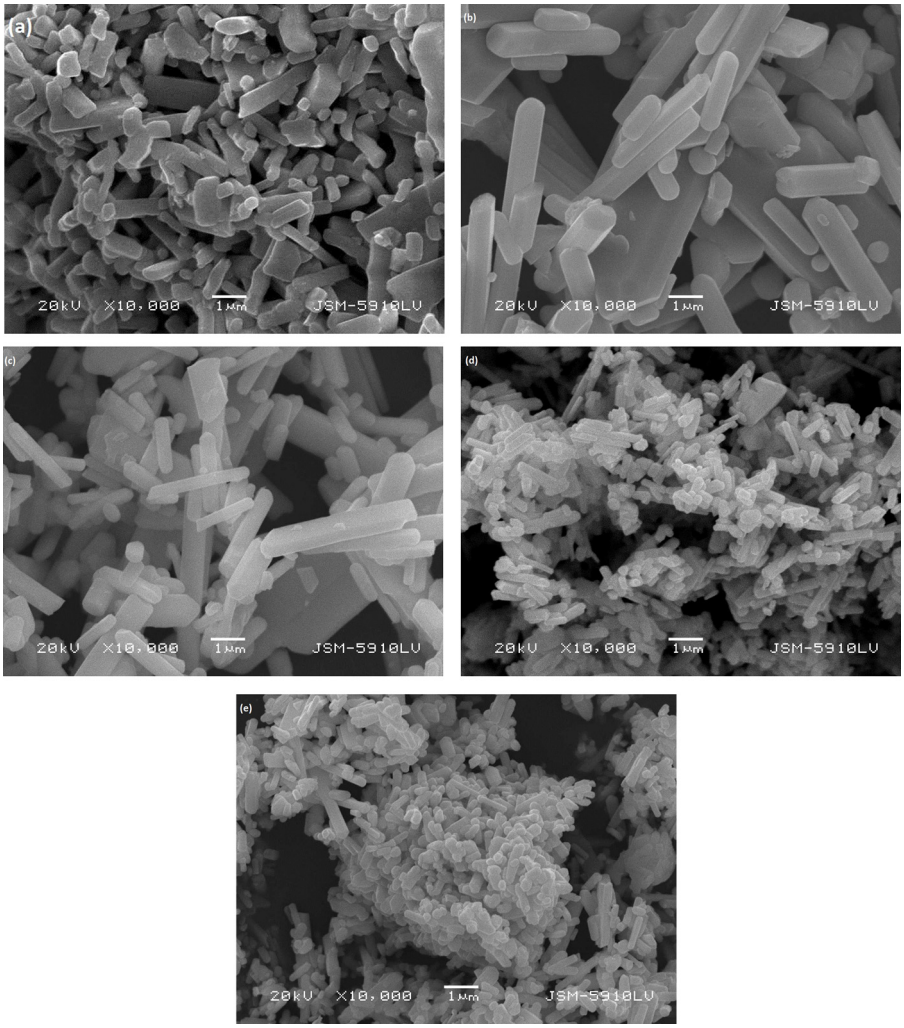

Fig. 2. The SEM picture of the pure (a), and 0.5 mol% (b), 1.0 mol% (c), 3.0 mol% (d), 6.0 mol% (e) Er^{3+} doped $CdNb_2O_6$ columbite powders calcined at 900 °C for 4 h.

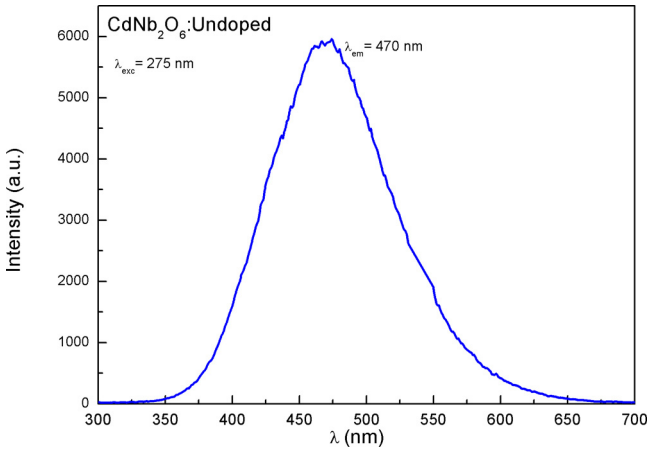

Fig. 3. Emission spectra of a visible room-temperature luminescence from pure powder.

3. Results and discussion

3.1. Morphology of the powders

The XRD patterns of all the $CdNb_2O_6$ compounds having different concentrations of Er^{3+} ions are given in Fig. 1. Each spectrum shows a good crystalline with an intense and narrow primary peak located at $2\theta = 18.7^{\circ}$ indicating that there is no effect of the Er^{3+} concentration on the formation of the crystalline phases in these compounds. The crystal structure and phase of all samples were analyzed by using these patterns. The orthorhombic $CdNb_2O_6$ columbine structure (space group P_{bcn60}) was identified by comparing the peak positions and the intensities with those in the Joint Committee on Powder Diffraction Standards (JCPDS) data files. It was clearly seen that the peak positions correspond well to the standard card with number 38-1428 for all samples. Moreover, undefined second phase formation observed at 3.0 mol% Er doping and its content increased with increasing doping concentration of Er^{3+} ions.

Fig. 2(a–e) shows the SEM images of pure and Er^{3+} doped $CdNb_2O_6$ compounds. The image of pure compound in Fig. 2(a) shows a clustered structure with different shapes. The image of the compound doped with Er^{3+} ions in Fig. 2(b–e) on the other hand shows the formation of a rod-like structure with relatively uniform

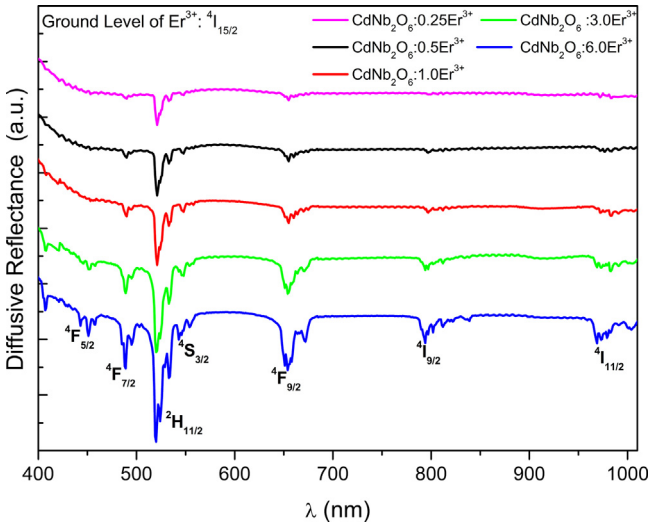

Fig. 4. Diffusive reflection spectra of the Er^{3+} doped powders.

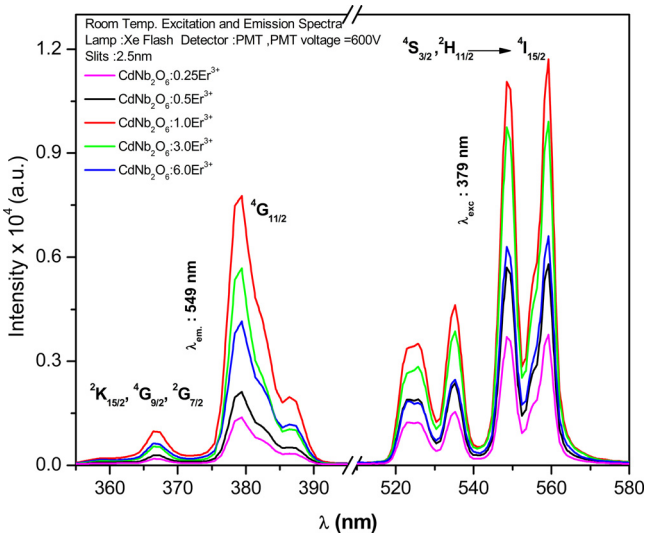

Fig. 5. Excitation and emission spectra of a visible room-temperature Er^{3+} ions luminescence from powders.

distribution. It is clearly seen from the SEM images that the particle sizes and the shapes of the samples are strongly affected by the presence of the Er^{3+} ions in the doped compounds. Also SEM images confirmed that the average particle sizes of Er^{3+} doped $CdNb_2O_6$ decreased with increasing doping concentration of Er^{3+} ions from about 3 μm to 300 nm.

3.2. Spectroscopic properties of the powders

The optical characterization of the pure and Er^{3+} doped of $CdNb_2O_6$ compounds was carried out by photoluminescence and photoluminescence excitation measurements. The luminescence spectrum of the pure compound measured upon 275 nm excitation is shown in Fig. 3. The spectrum consists of a broad band ranging from 350 to 700 nm which covers almost the entire visible spectral region.

The Diffuse reflectance spectra of the Er^{3+} doped of $CdNb_2O$ samples are shown in Fig. 4. The dips corresponding to the absorption lines observed in the wavelength range of 400–

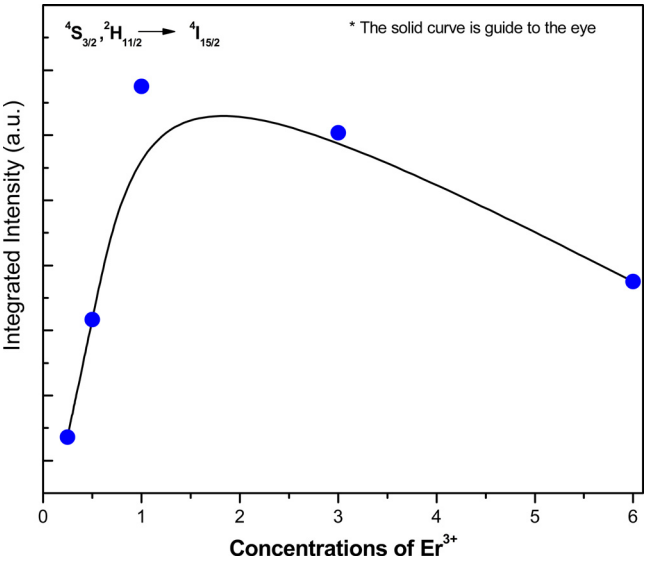

Fig. 6. Variation of integrated luminescence intensity of the transitions from the levels $^4S_{3/2}$,$^2H_{11/2}$ to the ground level $^4I_{15/2}$ for Er^{3+} doped powders.

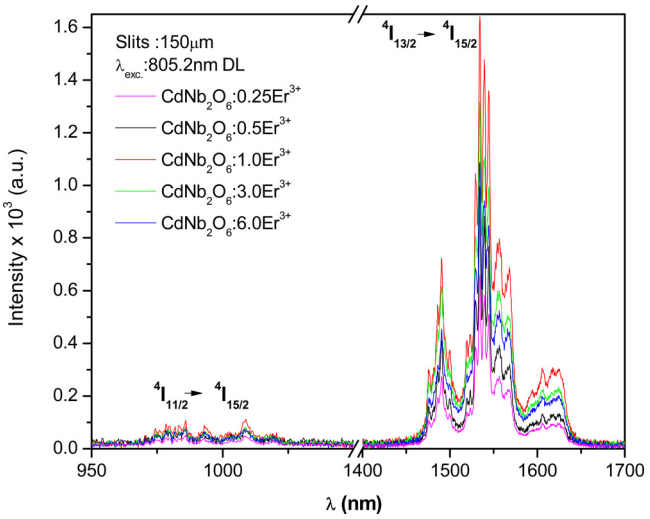

Fig. 7. Emission spectra of the phosphor powders for the $^4I_{11/2} \rightarrow {}^4I_{15/2}$, and $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transitions in $CdNb_2O_6$ powders doped with Er^{3+} at 300 K.

1000 nm are due to the f–f transitions from the $^4I_{15/2}$ ground level to excited levels of the Er^{3+}. The intensities of the dips were observed to increase linearly with concentration of Er^{3+} ions as can be seen in Fig. 4.

Fig. 5 shows the room temperature luminescence spectra of Er^{3+} ions measured in the visible wavelength region by exciting the level $^2H_{9/2}$ at 379 nm. Two different transitions were observed corresponding to the transitions from the levels $^4S_{3/2}$, $^2H_{11/2}$ to the ground level $^4I_{15/2}$. The variation of integrated luminescence intensity for Er^{3+} doped powders are presented in Fig. 6. As can be seen from the figure, concentration quenching was observed to occur above 1.0 mol% Er^{3+} concentration.

Fig. 7 presents the luminescence spectra of all Er^{3+} doped samples in the wavelength range of 900–1700 nm. Each spectrum contains two transitions from the $^4I_{11/2}$ to $^4I_{13/2}$ and the ground level, ($^4I_{15/2}$) within the 4f shell of the Er^{3+} ions. The emissions corresponding to the $^4I_{11/2} \rightarrow {}^4I_{15/2}$, and $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transitions are centered at about 0.98 μm and 1.55 μm. The J-manifolds of Er^{3+} ions are split due to the local symmetry of the $CdNb_2O_6$ cation sites; the spectral profile and the number of the stark components are the same for all the powders. This behavior can be explained as due to the fact that the local symmetry of ligand ions surrounding the Er^{3+} ions is the same for all samples because of the same crystalline phase. In addition, the emission intensities of the spectral lines for the $^4I_{11/2} \rightarrow {}^4I_{15/2}$, $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transitions increase with increasing Er^{3+} concentration below 1.0 mol% and starts decreasing for higher Er^{3+} concentrations.

4. Conclusions

Using the molten salt method, cadmium niobate phosphors activated with Er^{3+} were synthesized and annealed at 900 °C for 4 h. XRD patterns indicate that the crystalline formed is not affected by the presence of Er^{3+} ions in the 0–6.0 mol% concentration range. The average crystalline sizes estimated from SEM image are found to be affected by the Er^{3+} concentration. The average crystallite sizes were determined to decrease from 3 μm to 300 nm as the Er^{3+} concentration increased in the $CdNb_2O_6$ powders.

The intensity of the dips corresponding to the absorption lines measured from the reflectance spectra increase linearly with the concentration of Er^{3+} ions in these powders. Luminescence measurements carried out at room temperature clearly show that the intensities of the luminescence lines increase with increasing Er^{3+} concentration below 1.0 mol% and starts decreasing for higher Er^{3+} concentrations due to the existence of the concentration quenching processes.

Acknowledgment

This study was financially supported by the Scientific Research Project Commission (BAPKO) of Marmara University with the project number FEN-D-100413-0132.

References

[1] B.M. Tissue, Synthesis and luminescence of lanthanide ions in nanoscale insulating hosts, Chem. Mater. 10 (1998) 2837–2845.
[2] M. Erdem, G. Özen, C. Tav, B.D. Bartolo, Structural and spectroscopic properties of Nd^{3+}:$Y_2Si_2O_7$ phosphors, Ceram. Int. 39 (2013) 6029–6033.
[3] D. Hreniak, A. Speghini, M. Bettinelli, W. Strek, Spectroscopic investigations of nanostructured LiNbO3 doped with Eu^{3+}, J. Lumin. 119–120 (2006) 219–223.
[4] R.S. Chalihaa, K. Annapurnaa, A. Tarafder, V.S. Tiwari, P.K. Gupta, B. Karmakar, Structure, dielectric and optical properties of transparent Nd^{3+}: $KNbO_3$ nanocrystalline glass–ceramics, Opt. Mater. 32 (2010) 1202–1209.
[5] J. Huang, L. Zhou, Z. Liang, F. Gong, J. Han, R. Wang, Promising red phosphors $LaNbO_4$:Eu^{3+}, Bi^{3+} for LED solid-state lighting application, J. Rare Earths 28 (2010) 356–360.
[6] J.P. Cummings, S.H. Simonsen, The crystal structure of calcium niobate ($CaNb_2O_6$), Am. Mineral. 55 (1970) 90–97.
[7] M.T. Vanderborre, E. Husson, Comparison of the force field in various pyrochlore families II. Phases presenting structural defects, J. Solid State Chem. 53 (1984) 253–259.
[8] Y.J. Hsiao, Y.S. Chang, G.J. Chen, Y.H. Chang, Synthesis and the luminescent properties of CdNb2O6 oxides by sol–gel process, J. Alloys Compd. 471 (2009) 259–262.
[9] G. Blasse, M.G.J. van Leur, Luminescence and energy transfer in the columbite structure, Mater. Res. Bull. 20 (1985) 1037–1045.
[10] H. Brittain, W.A. McAllister, Luminescence of Eu(III) activated niobates, Spectrochim. Acta Part A: Mol. Spectrosc. 41 (1985) 1041–1046.