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Molten salt synthesis and spectral properties of Nd^{3+} doped $CdNb_2O_6$ columbite phosphors

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ABSTRACT

Pure and Nd-doped $CdNb_2O_6$ particles have been prepared by a molten salt method using cadmium nitrate, niobium oxide and Li_2SO_4–Na_2SO_4 salt mixture as a flux at a relatively low temperature as compared to solid-state reaction method. X-ray diffraction patterns of the pure $CdNb_2O_6$ samples exhibited a single orthorhombic phase. Photoluminescence (PL) properties of all the undoped and Nd-doped samples in visible and near-infrared spectral region were studied in detail. While a strong blue emission band centered at 460 nm at room temperature was observed for the pure $CdNb_2O_6$, additional characteristic luminescence of Nd^{3+} at 1.06 μm was observed for Nd-doped $CdNb_2O_6$. Concentration quenching phenomenon was detected depending on the Nd-doping concentrations at both room and relatively low temperatures. This characteristic of the doped samples may be ascribed to the energy transfer between Nd^{3+} and niobate groups (NbO_6).

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1. Introduction

High purity, compositionally uniform, single phase, small and uniform particle size powders are required for high resolution and high luminous efficiency of the optical materials in photonic device developments. Moreover, it should be pointed out that the selection of host lattices and active centers for such an optical material is important.

The columbite niobates MNb_2O_6 (M = Co, Cd, Ni, Mg, Cu, Zn, and Mn) having orthorhombic unit cell and space group Pbcn (60) [1] are known as interesting photoactive host materials due to their high refractive index (for $CaNb_2O_6$, n = 2.07–2.2) and, chemical stability [2]. The structure of MNb_2O_6 columbite consists of two kinds of octahedra as MO_6 and NbO_6. These two octahedras constitute independent repeating zig–zag chains by sharing edges and the chains are connected by sharing corners to form columbite structure [3]. Moreover, the columbite host matrix activated with the rare earth (RE^{3+}: Tb^{3+}, Eu^{3+}, Dy^{3+}, Yb^{3+}, Tm^{3+}, Nd^{3+}, Er^{3+}, Pr^{3+}) ions makes a promising candidate for red emission phosphor and, laser material in photonic applications [4–10]. 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 [11]. Although a few papers have been devoted to the study of undoped and rare earth doped cadmium niobate in the literature [11,12] no studies were made on the Nd-doped cadmium niobate materials.

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 solid-state reaction [13]. These features make the molten salt process a promising method since it results in improved sinterability [14–16].

In the present study, it was aimed to produce neodymium (Nd^{3+}) doped cadmium niobate ceramics by the molten salt technique and investigate into structural and luminescence properties in order to explore its potential application in photonic devices. To our knowledge this is the first report on structural and spectroscopic characterization of cadmium niobate ceramic activated with Nd^{3+} using molten salt synthesis.

2. Experimental

Undoped and doped $CdNb_2O_6$ columbite ceramic powders were synthesized via molten salt route by mixing starting materials of cadmium nitrate ($Cd(NO_3)_2{\cdot}4H_2O$) and niobium oxide (Nb_2O_5) at a salt to oxide weight ratio of 1:1. Li_2SO_4–Na_2SO_4 salt mixture was used at molar ratio of 0.635/0.365. After mixing starting materials (cadmium nitrate, niobium oxide and neodymium oxide) in an agate mortar and Li_2SO_4 and Na_2SO_4 in an another mortar, they were mixed well to provide homogeneity. After calcining sufficient amount of mixture at 900 °C for 4 h in an alumina

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crucible, they were washed with ultra pure water and vacuum filtered several times to remove ionic salts from the oxides. The presence of the sulphate ions in filtrate were checked by using qualitative reactions.

The surface morphology and microstructure of powders were examined by scanning electron microscopy (SEM; Jeol JSM 5910LV) equipped with EDS (Oxford Instruments Inca X-Sight 7274). X-ray diffraction patterns of powders were obtained using Rigaku Rotaflex model RU200B diffractometer using Cu Kα radiation ($\lambda = 1.546$ Å) with a step size of 0.02° in the 2θ range of 15–60°.

Emission spectra of the powders doped with Nd^{3+} ions were measured in the wavelength-range of 850–1150 nm and temperature range of 45–300 K under 800 nm excitation from a diode laser (LDI-820). Fluorescence from the samples were focused on the slit of a Monochromator (Mc Pearson Model 2051) and detected by PMT (Hamamatsu 7102) detector. For the decay measurements a Ti: Sapphire Laser (Schwartz-SEO Electrooptics Co.) was used as excitation source. The pulse duration was 10 ns and the repetition rate was 10 Hz. The temporal evolution of the signal was recorded using a Tektronix Model 380 oscilloscope. All the measurements were carried out at the range of 45–300 K temperature using a Janis model closed cycle refrigerator.

3. Results and discussions

3.1. Structural characterization

Fig. 1 shows the XRD patterns of $CdNb_2O_6$ powders synthesized by molten salt synthesis at 900 °C for 4 h. Synthesis of undoped and 0.5, 3, and 6 mol% Nd-doped $CdNb_2O_6$ powders via molten salt route by using the salt/oxide molar ratio of 1:1 gave orthorhombic single phase $CdNb_2O_6$ (JCPDS: 38-1428). No any other second phases were observed in the XRD.

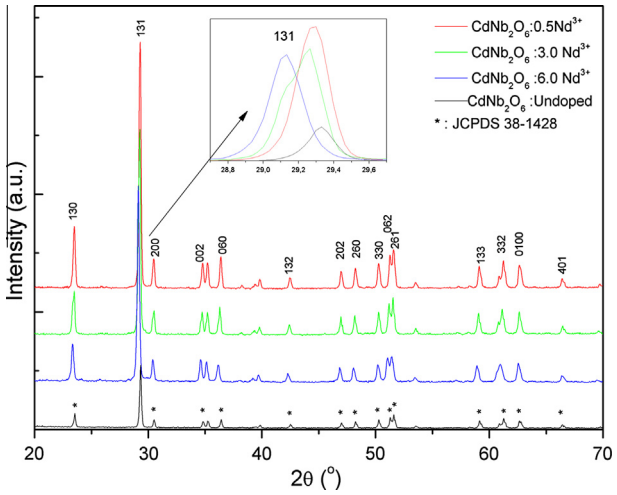

Fig. 1. XRD pattern of $CdNb_2O_6$ powder doped with different amount of Nd^{3+} and synthesized with molten salt method of 900 °C for 4 h.

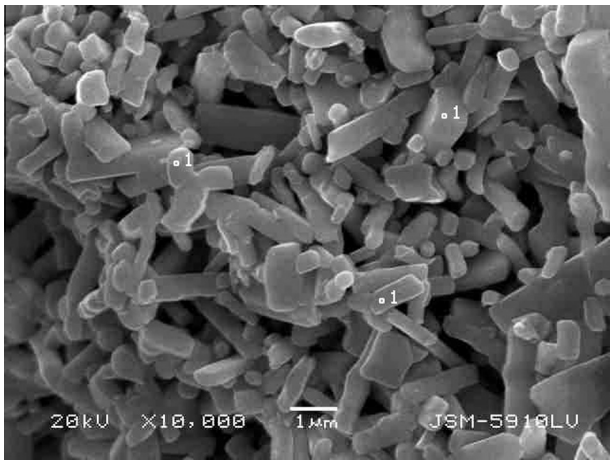

Fig. 2. The SEM picture of the pure $CdNb_2O_6$ columbite powders calcined at 900 °C for 4 h. Point (1) indicates the $CdNb_2O_6$ phase.

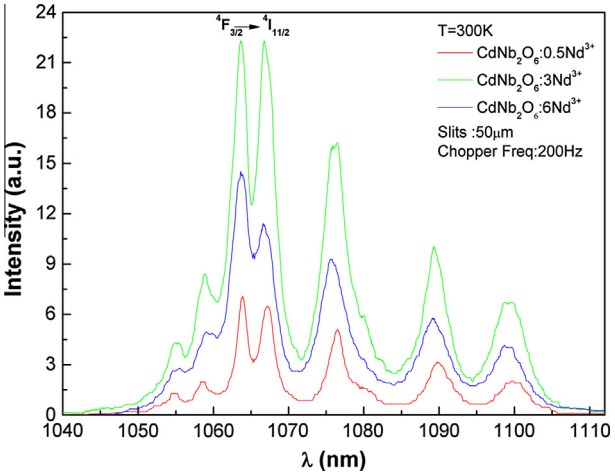

Fig. 3. Emission spectra of the phosphor powders for the $^4F_{3/2} \rightarrow {}^4I_{11/2}$, $^4I_{9/2}$ transition in $CdNb_2O_6$ powders doped with Nd^{3+} at 300 K.

A remarkable shift to lower angles was observed for (1 3 1) peak for the high Nd^{3+} concentrations. These peak shifts indicate the presence of strains in the doped host lattices due to the doping of Nd^{3+} cation which has slightly larger ionic radii than Cd^{2+} (0.98 Å for Nd^{3+} and 0.95 Å for Cd^{2+} [17].

The SEM image of the undoped $CdNb_2O_6$ powder is illustrated in Fig. 2. As its seen from the SEM micrograph, single phase with irregular rod-like morphology was observed. EDS analysis from the particles signed with 1 number in the SEM image also indicated that the atomic weight ratio of the elements were in agreement with the theoretical compositions of $CdNb_2O_6$.

3.2. Emission spectra and decay patterns

Luminescence measurements measured upon 800 nm excitation contains two bands corresponding to the transitions from

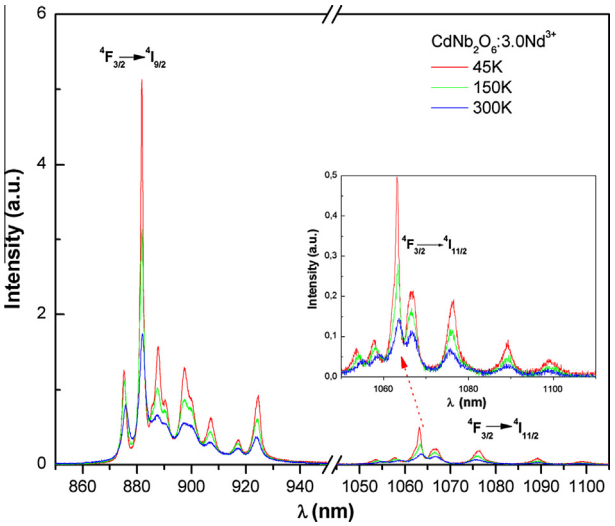

Fig. 4. Emission spectra of 3 mol%:Nd^{3+} doped $CdNb_2O_6$ for the $^4F_{3/2} \rightarrow {}^4I_{11/2}$, $^4I_{9/2}$ transition in Nd^{3+} ions at 45–300 K.

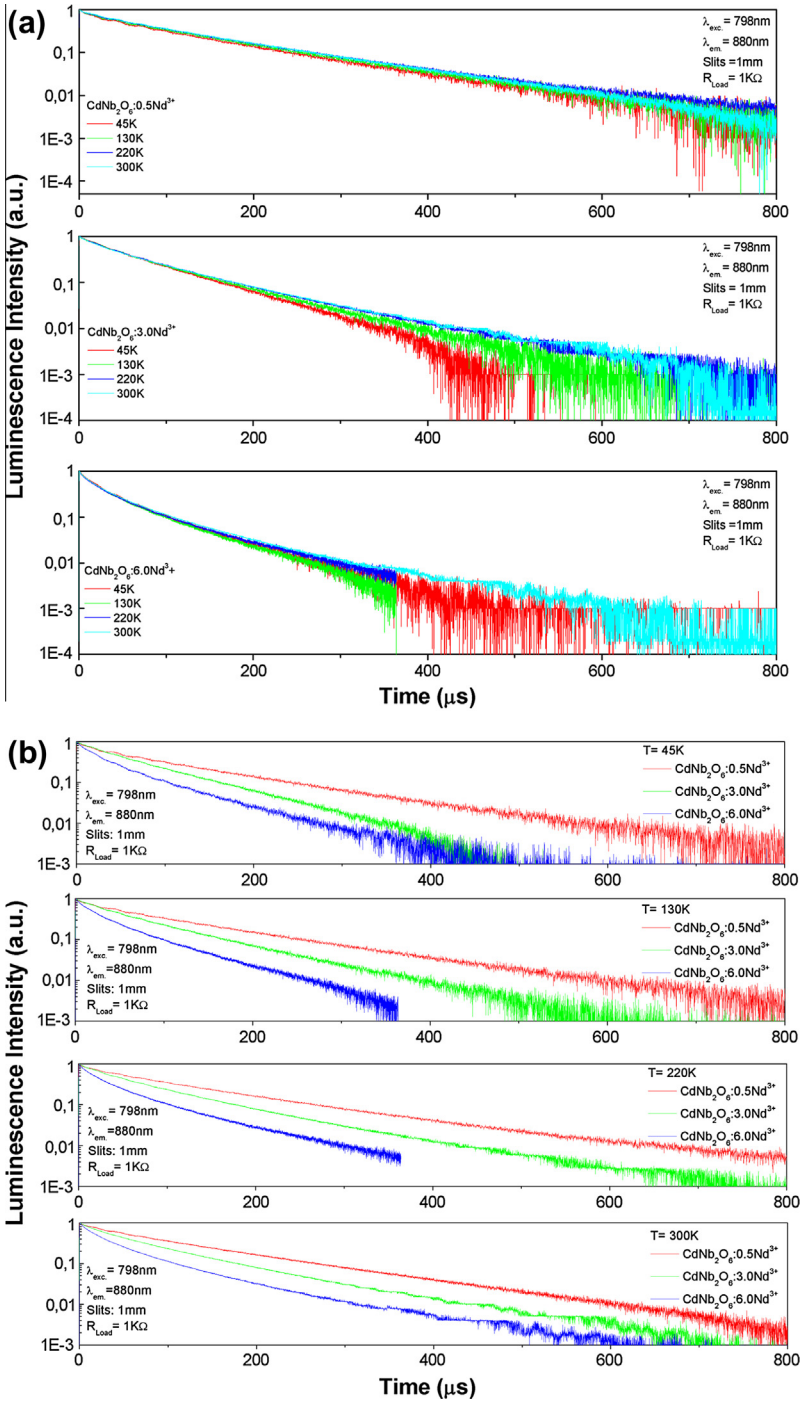

Fig. 5. (a) Decay curves of the $^4F_{3/2}$ emission measured at various temperatures (45–300 K) for different Nd^{3+} concentration. (b) Decay curves of the $^4F_{3/2}$ emission for different Nd^{3+} concentrations at various temperatures between 45 and 300 K.

the $^4F_{3/2}$ to $^4I_{11/2}$ and $^4I_{9/2}$ levels. Emission spectra of the laser transition at 1062 nm due to the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition measured at 300 K are shown in Fig. 3.

As it can be seen from the emission spectra it was found that the *J*-manifolds of Nd^{3+} ions were split due to symmetry of $CdNb_2O_6$ cation sites and the spectral profile and the number of the Stark components were the same for the three powders. This behavior can be explained from the fact that the local symmetry of ligand ions surrounding of Nd^{3+} ions were same for the samples. It can also be seen from Fig. 3 that concentration quenching occurred Nd^{3+} ions in the powder was 6.0 mol% of Nd^{3+} concentration.

Fig. 4 shows the temperature effect on the spectral profiles of the emission lines and the band widths for the $^4F_{3/2} \rightarrow {}^4I_{11/2}$, $^4I_{9/2}$ transitions in $CdNb_2O_6$ powders doped with 3 mol%:Nd^{3+} ions. The inset in the figure corresponds to the wavelength-range of 1000–1150 nm. Luminescence intensity of both emission bands decreased with temperature from 45 to 300 K.

The decay patterns of $^4F_{3/2}$ level were measured by monitoring the emission due to the $^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition of Nd^{3+} ions in the powders using the laser beam with the excitation wavelength 798 nm. The decay curves measured at various temperatures between 45 and 300 K are illustrated in Fig. 5(a and b).

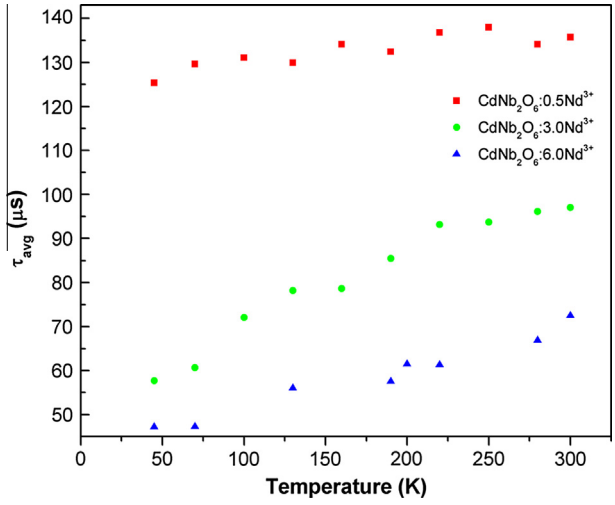

Fig. 6. Average decay times of the $^4F_{3/2}$ emission as a function of temperature.

The analysis of these curves explained the effect of temperature and Nd^{3+} ion concentration on the luminescence properties. As it can be seen from the figures, the decay patterns measured as a function of temperature was dependent on the Nd^{3+} concentration. The decay become faster as the Nd^{3+} concentration increased at all temperatures. Decay patterns for all Nd^{3+} concentrations were observed to be non-exponential at all temperatures indicating the interaction between the Nd^{3+} ions leading the energy transfer processes. Since the decay patterns were non-exponential at all temperatures, the average decay times of the $^4F_{3/2}$ emission as a function of temperature were determined using the decay patterns given in Fig. 6.

Average lifetime was calculated using to the relation $\tau_{avg} = \int \frac{I}{I_o} dt$ where I_o is the initial fluorescence intensity measured right after the excitation occurred. The lifetime of $^4F_{3/2}$ level becomes shorter as the concentration of the Nd^{3+} increased in $CdNb_2O_6$ crystalline powders (Fig. 6).

Fig. 6 also shows the effect of temperature on the average lifetime of Nd^{3+} ions. The average lifetime of the $^4F_{3/2}$ level was found to be almost independent of temperature of 0.5 mol%, while the lifetime of the same level was observed to increase with temperature in samples doped with 3 and 6 mol% Nd^{3+} ions. The increase of lifetime with temperature might indicate that the radiative energy transfer processes become dominant as the Nd^{3+} concentration increases.

4. Conclusion

Undoped and Nd-doped $CdNb_2O_6$ crystalline powders were successfully synthesized by molten salt synthesis method at a relatively low temperature than that of the other traditional conventional methods. XRD analysis showed that undoped and Nd^{3+} doped powders were single phased with orthorhombic structure. The luminescence properties of the powders indicated the concentration quenching occurs when the concentration of Nd^{3+} ions in the powder was 6.0 mol%. The decay patterns measured as function of temperature depend on the Nd^{3+} concentration. The decay becomes faster as the Nd^{3+} concentration increases at all temperatures. Decay patterns for all Nd^{3+} concentrations are observed to be non-exponential at all temperatures indicating the interaction between the Nd^{3+} ions leading the energy transfer processes. The average lifetime of the $^4F_{3/2}$ level was seen to be nearly independent of temperature in low Nd^{3+} concentration (0.5 mol%) while the lifetime of the same level was observed to increase with temperature in both samples doped with 3 and 6 mol% Nd^{3+} ions.

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