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## Judd–Ofelt parameters and X-ray irradiation results of $MNb_2O_6:Eu^{3+}$ ( $M = Sr, Cd, Ni$ ) phosphors synthesized via a molten salt method

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Trivalent Eu-activated  $MNb_2O_6$  ( $M = Sr, Cd, Ni$ ) ceramic phosphors were produced using the molten salt route, which involves a low sintering temperature and provides improved homogeneity. The photoluminescence (PL) and radioluminescence (RL) spectra of phosphors exhibited characteristic  $Eu^{3+}$  emissions with  $^5F_0 \rightarrow ^7F_j$  transitions, and strong peaks occurred at the  $^5D_0 \rightarrow ^7F_2$  transition. The PL and RL emissions of  $SrNb_2O_6:Eu^{3+}$  decreased over 3 mol%, while both emissions for  $CdNb_2O_6:Eu^{3+}$  and  $NiNb_2O_6:Eu^{3+}$  increased with increasing  $Eu^{3+}$  concentration. The spectral properties of phosphors were evaluated by determining Judd–Ofelt intensity parameters ( $\Omega_2, \Omega_4$ ) from the PL emission spectrum. The quantum efficiencies ( $\eta_{QE}\%$ ) of  $MNb_2O_6:Eu^{3+}$  ( $M = Sr, Cd, Ni$ ) phosphors with the highest emission were found as 61.87%, 41.89%, and 11.87% respectively. Bandwidths ( $\sigma_e \times \Delta\lambda_{eff}$ ) and optical gains ( $\sigma_e \times \tau$ ) of  $MNb_2O_6:Eu^{3+}$  ( $M = Sr, Cd, Ni$ ) phosphors with highest emissions were found as follows;  $24.182 \times 10^{-28}$ ,  $28.674 \times 10^{-28}$ ,  $38.647 \times 10^{-28} \text{ cm}^3$  and  $20.441 \times 10^{-25}$ ,  $13.790 \times 10^{-25}$ ,  $3.987 \times 10^{-25} \text{ cm}^2 \text{ s}$ , respectively, corresponding to the  $^5D_0 \rightarrow ^7F_2$  transition.

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### 1. Introduction

The scientific and technological applications of rare earth (RE) elements have seen significant progress in last few decades due to their unique spectroscopic properties in different host lattices, where their superior chemical and thermal stability are along with their outstanding luminescent yield and color purity. Today, trivalent RE ions have a wide range of applications, such as high-performance luminescent devices, magnets, catalysts, and other functional materials.<sup>1–7</sup> When the host lattice is activated by RE<sup>3+</sup> ions, besides PL, they can cause changes in RL features. In the radioluminescence mechanism, high-energy ionizing radiation (X-rays, alpha particles, and electrons) instantly transforms into thousands of low-energy photons (1–6 eV). The RL feature is of great importance in many fields, such as high-tech industrial applications, homeland security, radiography, biochemical applications, medical devices, biological safety, particle physics, astrophysics, and nuclear material applications.<sup>6,7</sup>

The oxide compounds of columbite niobates can be expressed as  $MNb_2O_6$  ( $M = Sr, Cd, Ni, Co, Mg, Mn, etc.$ ). The symmetry of  $MNb_2O_6$  easily accepts guest ions of a similar ionic size as the metal and Nb ions of the structure. As the  $MNb_2O_6$

structure, the strontium niobate ( $SrNb_2O_6$ ) compound composed of the  $SrO_6$ – $NbO_6$  octahedral<sup>8,9</sup> stands out due to its luminescence,<sup>7–9</sup> photocatalytic,<sup>10,11</sup> and dielectric<sup>12</sup> properties. The high photocatalytic property of  $SrNb_2O_6$  is attributed to its increasing absorption by the change of its crystal structure.<sup>10</sup> The molten salt method, one of the methods used in the synthesis of niobates has a favorite feature due to some advantages, which provides a low sintering temperature, short reaction time, good composition, and improved homogeneity.<sup>7,8</sup> The advantage of the molten salt method can be evaluated by comparing it with the solid-state reaction method. Here,  $SrNb_2O_6$  was produced by the solid-state reaction method at 1250 °C for 7 h,<sup>9</sup> whereas  $SrNb_2O_6$  was fabricated using the molten salt method at 650 °C for 4 h.<sup>7,8</sup>

In this study, the structural, photoluminescence, and X-ray induced characterizations of  $SrNb_2O_6:Eu^{3+}$  were carried out by XRD, SEM, PL, and RL analyses. In addition, the previously reported phosphors of  $CdNb_2O_6:Eu^{3+}$  (ref. 13) and  $NiNb_2O_6:Eu^{3+}$  (ref. 14) were included in the study, and the Judd–Ofelt intensity parameters and radioluminescence results of  $MNb_2O_6:Eu^{3+}$  ( $M = Sr, Cd, Ni$ ) phosphors were reported by comparison with PL and RL analyses. Also, the grain structures of three compounds were examined by SEM analysis.

### 2 Experimental

In the synthesis of  $(Sr, Cd, Ni)Nb_2O_6:xEu^{3+}$  ( $x\% = 0.5, 3, 6 \text{ mol\%}$ ) and undoped ceramic powders by the molten salt method, as starting materials for each synthesis, strontium

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nitrate ( $\text{Sr}(\text{NO}_3)_2$ ) (Sigma-Aldrich, 99%), cadmium nitrate tetrahydrate ( $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ) (Sigma-Aldrich, 98.5%), nickel nitrate hexahydrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) (Sigma-Aldrich, 99%), pure niobium oxide ( $\text{Nb}_2\text{O}_5$ ) (Alpha Aesar, 99.9%), and  $\text{Eu}_2\text{O}_3$  (Alpha Aesar, 99.9%) powder were used in the calculated stoichiometric amounts. The  $x$  value was taken as “mol”, which means 2 Eu atoms due to the  $\text{Eu}_2\text{O}_3$  compound. The syntheses of  $(\text{Cd},\text{Ni})\text{Nb}_2\text{O}_6:\text{Eu}^{3+}$  (ref. 13 and <sup>14</sup>) and  $\text{SrNb}_2\text{O}_6:\text{Nd}^{3+}$ ,  $\text{Dy}^{3+}$  (ref. 7 and <sup>8</sup>) were reported as intermediate solid solutions. However, the  $\text{Sr}(\text{NO}_3)_2$  amount was reduced slightly to prevent secondary phase formation in the synthesis of  $\text{SrNb}_2\text{O}_6:\text{Nd}^{3+}$ ,  $\text{Dy}^{3+}$ <sup>7,8</sup> similarly, 0.98 and 0.95 mol were used instead of 1 mol  $\text{Sr}(\text{NO}_3)_2$  for the 3 and 6 mol%  $\text{Eu}^{3+}$  samples, respectively, corresponding to 2 mol of  $\text{Nb}_2\text{O}_5$ . The stoichiometric amounts of the molten salt mixtures were added to the reactant mixtures. For this purpose, the molten salts to be used and their mixing ratios were, respectively, for strontium niobate synthesis,  $\text{NaCl} : \text{KCl}$ , salt : salt molar ratio 6 : 1 and salt : oxide weight ratio 1 : 1, for cadmium niobate synthesis,  $\text{Li}_2\text{SO}_4 : \text{Na}_2\text{SO}_4$ , salt : salt molar ratio 1 : 1 and salt : oxide weight ratio 1 : 1, for nickel niobate synthesis,  $\text{Li}_2\text{SO}_4 : \text{Na}_2\text{SO}_4$ , salt : salt molar ratio 1 : 1 and salt : oxide weight ratio 1 : 1. The starting materials for each compound group were mixed to produce the phosphor powders by the molten salt synthesis method and finely ground in an agate mortar to ensure homogeneity. After that, europium oxide ( $\text{Eu}_2\text{O}_3$ ) dopant was added. The final powder mixture was thoroughly mixed in an agate mortar for a final time and reground to ensure greater homogeneity. Then, mixtures prepared by weighing for each compound were placed and calcined in alumina crucibles at 650 °C for 4 h for strontium niobate, or at 900 °C for 4 h for cadmium niobate and nickel niobate. Phosphor powders obtained as a result of the heat treatment were washed many times with ultrapure water to remove the ionic salts they contained and vacuum filtered several times. The presence of Cl-ions in the filtrate was checked using qualitative reactions.

The powder samples analyses were carried out by XRD (X-ray diffractometer; D2 PHASER, Bruker Corp., Germany) using  $\text{Cu}-\text{K}_\alpha$  (1.54 Å) radiation in between  $2\theta = 5\text{--}70$  °C with a scan speed of 2 °C min<sup>-1</sup>. SEM micrographs of the samples were taken by scanning electron microscopy (SEM; Inspect S50, FEI Corp., USA) after Au coating. Elemental compositions were determined by energy dispersive spectroscopy (EDS; INCAx-Sight 7274 model; 133 eV resolution 5.9 keV, OXFORD Instruments, England) which was attached to the SEM system (JSM-5910LV, JEOL Corp., Japan). EDS was performed at 20 kV SEM acceleration voltage.

PL (photoluminescence) measurements were recorded on an Edinburgh Instruments (UK) FLSP920 model fluorescence spectrometer with xenon lamp (450 W) continuous wavelength lamps for steady-state measurements. Decay times were taken by  $\mu\text{F1}$  and  $\mu\text{F2}$ : 5 W or 60 W pulsed xenon microsecond flashlamps producing short microsecond pulses for decay measurements. Decay curves data ( $B_1$ ,  $\tau_1$ ,  $B_2$ ,  $\tau_2$ ) were recorded with a time-correlated single-photon counting (TCSPC) system. Radioluminescence (RL) results were obtained using an Horiba Jobin Yvon spectrometer (Japan), which included a liquid nitrogen-cooled CCD detector and an X-ray irradiation source Machlett

OEG-50A. The data for the RL were recorded with a detector integration time of 5 s between 200–1000 nm and 2 mm was chosen for the slit widths (input and output). The operating level of the spectrometer was 30 kV and 15 mA (30 Gy min<sup>-1</sup>) and it was operated in a dark environment and at room temperature.

## 3. Results and discussions

### 3.1 Structural analyses

Fig. 1 shows the X-ray diffraction results of undoped  $\text{SrNb}_2\text{O}_6$  and  $\text{Eu}^{3+}$ -doped  $\text{SrNb}_2\text{O}_6$  samples. The XRD pattern (JCPDS no: 28-1243) of the samples was indexed by orthorhombic columbite symmetry with the space group  $Pb\bar{c}n60$ . The  $\text{CdNb}_2\text{O}_6:\text{Eu}^{3+}$  (ref. 13) and  $\text{NiNb}_2\text{O}_6:\text{Eu}^{3+}$  (ref. 14) structures also had the same symmetry, and their symmetry continued up to 6 mol%, while secondary phases were found at low amounts. The XRD-SEM results of  $\text{SrNb}_2\text{O}_6:\text{Eu}^{3+}$  were investigated in this study, the detailed X-ray diffraction results of the  $\text{CdNb}_2\text{O}_6:\text{Eu}^{3+}$  and  $\text{NiNb}_2\text{O}_6:\text{Eu}^{3+}$  have been reported in ref. 13 and <sup>14</sup>. The cell parameters of orthorhombic  $\text{SrNb}_2\text{O}_6$  are  $a = 5.592$  Å,  $b = 7.722$  Å,  $c = 10.989$  Å, and  $\alpha = \beta = \gamma = 90^\circ$ .<sup>7</sup> On the other hand, it has been reported that the orthorhombic columbite symmetry and monoclinic symmetry almost fully overlap with each other.<sup>15,16</sup> Accordingly, XRD reflections of  $\text{SrNb}_2\text{O}_6$  could be indexed with monoclinic symmetry (space group  $P2_1/c$ ) which exactly fitted with the orthorhombic symmetry.<sup>15,16</sup> Based on the monoclinic symmetry, the cell parameters of  $\text{SrNb}_2\text{O}_6$  are  $a = 5.594$  Å,  $b = 7.722$  Å,  $c = 10.986$  Å, and  $\alpha = 90.37^\circ$ ,  $\beta = \gamma = 90^\circ$ .<sup>17,18</sup>

The  $\text{SrNb}_2\text{O}_6$  structure composed of corner-shared and edge-shared  $\text{NbO}_6$  octahedral aligned along the  $a$ -axis and  $c$ -axis, respectively, as shown in Fig. 2. The  $\text{Sr}^{2+}$  and  $\text{Nb}^{5+}$  cations are surrounded by  $\text{O}^{2-}$  with 8 and 6 CN (coordination number), and their ionic radii ( $r$ ) are 1.26 Å and 0.64 Å, respectively.<sup>7,9</sup> There is a cationic site with Wyckoff position 4e for the compatibility of the activator ions within the crystal structure.<sup>9</sup> The  $\text{Eu}^{3+}$  ions

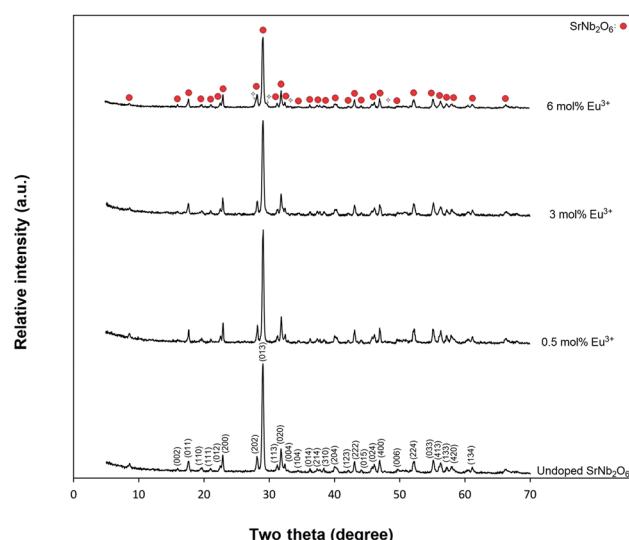


Fig. 1 X-ray diffraction results for undoped  $\text{SrNb}_2\text{O}_6$  and  $\text{Eu}^{3+}$ -doped  $\text{SrNb}_2\text{O}_6$  powders.

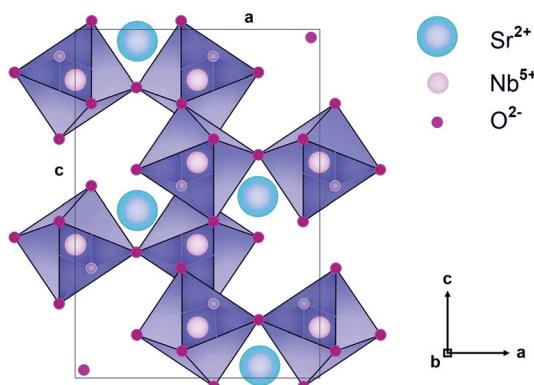


Fig. 2 Schematic illustration of  $\text{SrNb}_2\text{O}_6$  crystal in the direction of the  $b$  axis.

will occupy the  $\text{SrNb}_2\text{O}_6$  structure with the ionic radii of  $0.947\text{ \AA}$  for 6 CN and  $1.066\text{ \AA}$  for 8 CN. On the basis of  $\text{SrNb}_2\text{O}_6$  doping with  $\text{Eu}^{3+}$ , the  $\text{Eu}^{3+}$  ions will take place as an intermediate atom, while some  $\text{Eu}^{3+}$  ions will replace the ions of  $\text{Sr}^{2+}$ . A small amount of  $\text{Eu}^{3+}$  ions lead to the formation of a minor amount of  $\text{EuNbO}_4$  for 6 mol% sample, as seen in the XRD pattern in Fig. 1.

Also, the increase in positive charge due to the inclusion of  $\text{Eu}^{3+}$  ions will affect the lattice charge balance in the lattice.

SEM micrographs of  $\text{MNB}_2\text{O}_6:\text{Eu}^{3+}$  structures ( $\text{M} = \text{Sr, Cd, Ni}$ ) for 3 mol% concentration of  $\text{Eu}^{3+}$  are presented in Fig. 3(a-d). SEM micrographs of  $\text{Eu}^{3+}$ -doped  $\text{SrNb}_2\text{O}_6$  are given in Fig. 3(a and b) at  $2000\times$  and  $20\,000\times$  magnifications, respectively. The grain morphologies with rod-like shapes exhibited the characteristic structure of  $\text{SrNb}_2\text{O}_6$ .<sup>7,8</sup> The thicknesses and lengths of the rods for all the samples varied between  $0.06\text{--}0.68$  and  $0.21\text{--}12\text{ }\mu\text{m}$ , respectively. The grain shape and size of  $\text{CdNb}_2\text{O}_6:\text{Eu}^{3+}$  and  $\text{NiNb}_2\text{O}_6:\text{Eu}^{3+}$  differed in the SEM micrographs given in Fig. 3(c and d) and at  $20\,000\times$  magnification, respectively. While the grains of  $\text{Eu}^{3+}$ -doped  $\text{CdNb}_2\text{O}_6$  were irregular, agglomerated, and plate-like shape, the grain sizes varied in the range of  $0.5\text{--}4\text{ }\mu\text{m}$ . The grain morphologies of  $\text{Eu}^{3+}$ -doped  $\text{NiNb}_2\text{O}_6$  were round-like shape and relatively less agglomerated, with small grain sizes in the range of  $0.1\text{--}1\text{ }\mu\text{m}$ . The EDS spectra and elemental compositions (at% and wt%) for 3 mol%  $\text{Eu}^{3+}$ -doped  $\text{MNB}_2\text{O}_6$  ( $\text{M} = \text{Sr, Cd, Ni}$ ) samples are given in Fig. 4(a-c), respectively. The EDS atomic compositions (%) of the samples are highly compatible with the theoretical atomic values (%).

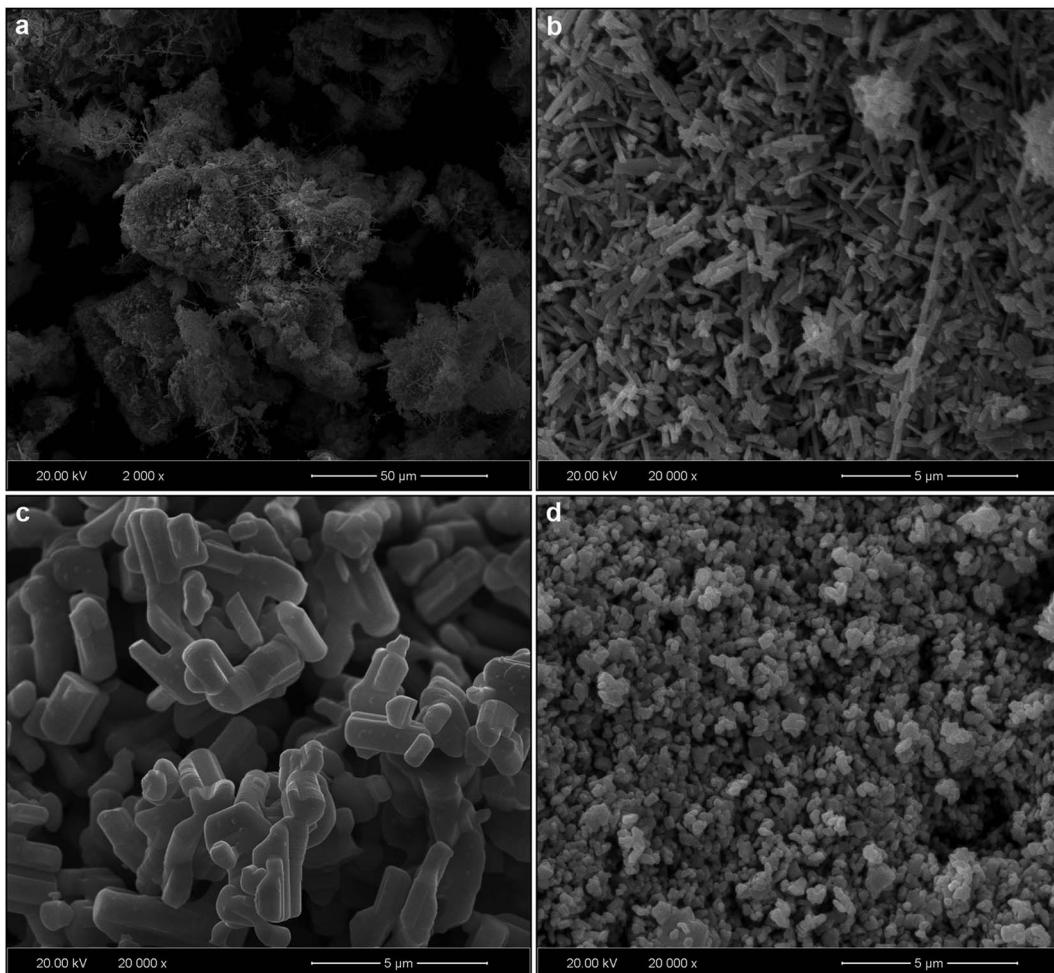


Fig. 3 SEM results of 3 mol%  $\text{Eu}^{3+}$ -doped  $\text{MNB}_2\text{O}_6$  samples: (a) SEM micrograph for  $\text{SrNb}_2\text{O}_6:\text{Eu}^{3+}$  at low ( $2000\times$ ) magnification, and SEM micrographs at high ( $20\,000\times$ ) magnification: (b)  $\text{SrNb}_2\text{O}_6:\text{Eu}^{3+}$ , (c)  $\text{CdNb}_2\text{O}_6:\text{Eu}^{3+}$ , and (d)  $\text{NiNb}_2\text{O}_6:\text{Eu}^{3+}$ .



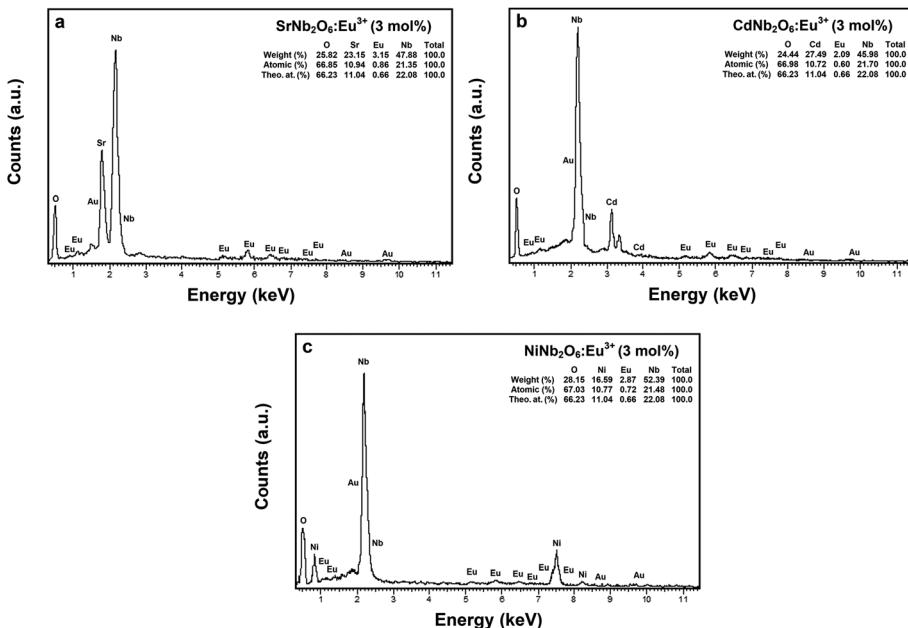


Fig. 4 EDS elemental compositions (wt%, at%) and theoretical atomic values (%) for 3 mol% Eu<sup>3+</sup>-doped MNb<sub>2</sub>O<sub>6</sub> samples: (a) SrNb<sub>2</sub>O<sub>6</sub>:Eu<sup>3+</sup>, (b) CdNb<sub>2</sub>O<sub>6</sub>:Eu<sup>3+</sup>, and (c) NiNb<sub>2</sub>O<sub>6</sub>:Eu<sup>3+</sup>.

### 3.2 Photoluminescence and radioluminescence analyses

Fig. 5(a–c) show the CT bands and PL excitations of MNb<sub>2</sub>O<sub>6</sub>:Eu<sup>3+</sup> (M = Sr, Cd, Ni) phosphors recorded at emission wavelengths of 615.7, 616.2, and 614.0 nm, respectively. PL excitations of the phosphors were assigned to the transitions of <sup>7</sup>F<sub>0</sub> → <sup>5</sup>D<sub>4</sub>, <sup>7</sup>F<sub>0</sub> → <sup>5</sup>G<sub>2</sub>, <sup>7</sup>F<sub>0</sub> → <sup>5</sup>L<sub>6</sub>, <sup>7</sup>F<sub>0</sub> → <sup>5</sup>D<sub>3</sub>, and <sup>7</sup>F<sub>0</sub> → <sup>5</sup>D<sub>2</sub>. The

broad CT bands with peak centers at 277.4 nm (SrNb<sub>2</sub>O<sub>6</sub>:Eu<sup>3+</sup>), 276.6 nm (CdNb<sub>2</sub>O<sub>6</sub>:Eu<sup>3+</sup>), and 277.7 nm (NiNb<sub>2</sub>O<sub>6</sub>:Eu<sup>3+</sup>) could be attributed to the Eu<sup>3+</sup>–O<sup>2-</sup> charge transfer, which results from the transition of 2p electrons of O<sup>2-</sup> to the empty 4f orbitals of Eu<sup>3+</sup> ion.<sup>5,6</sup> Fig. 6(a–c) show the PL emissions of MNb<sub>2</sub>O<sub>6</sub>:Eu<sup>3+</sup> (M = Sr, Cd, Ni) phosphors monitored at the <sup>5</sup>D<sub>0</sub>

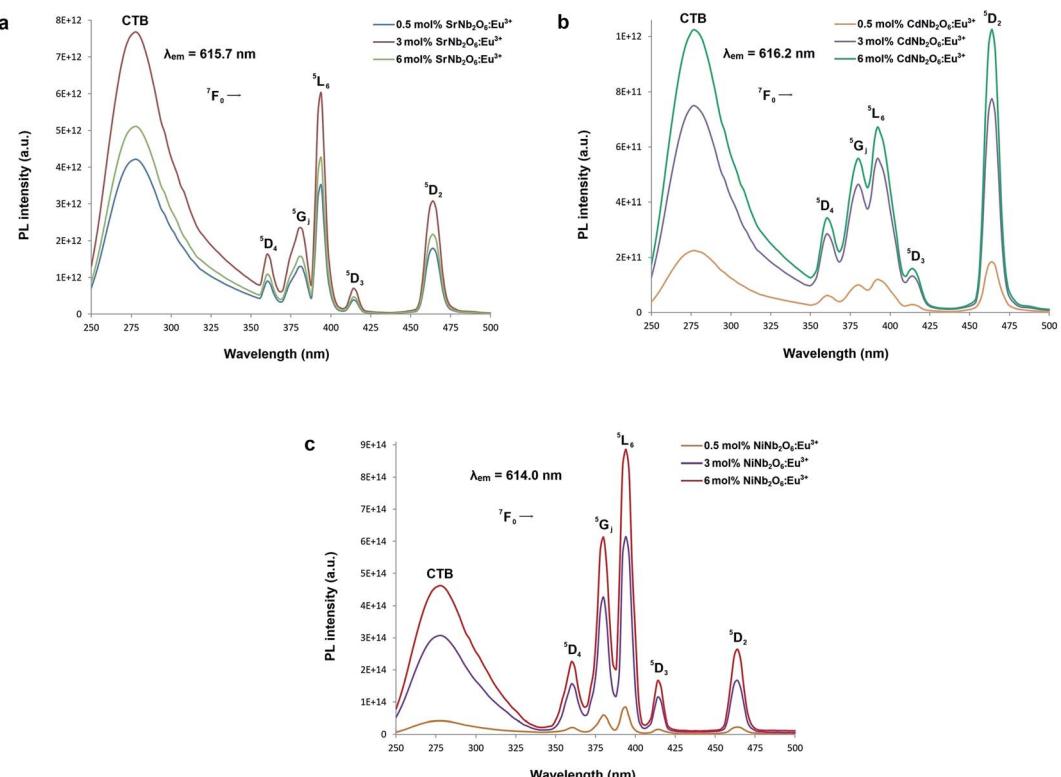


Fig. 5 PL excitation spectra and charge-transfer bands (CTB) of the phosphors: (a) SrNb<sub>2</sub>O<sub>6</sub>:Eu<sup>3+</sup>, (b) CdNb<sub>2</sub>O<sub>6</sub>:Eu<sup>3+</sup>, and (c) NiNb<sub>2</sub>O<sub>6</sub>:Eu<sup>3+</sup>.



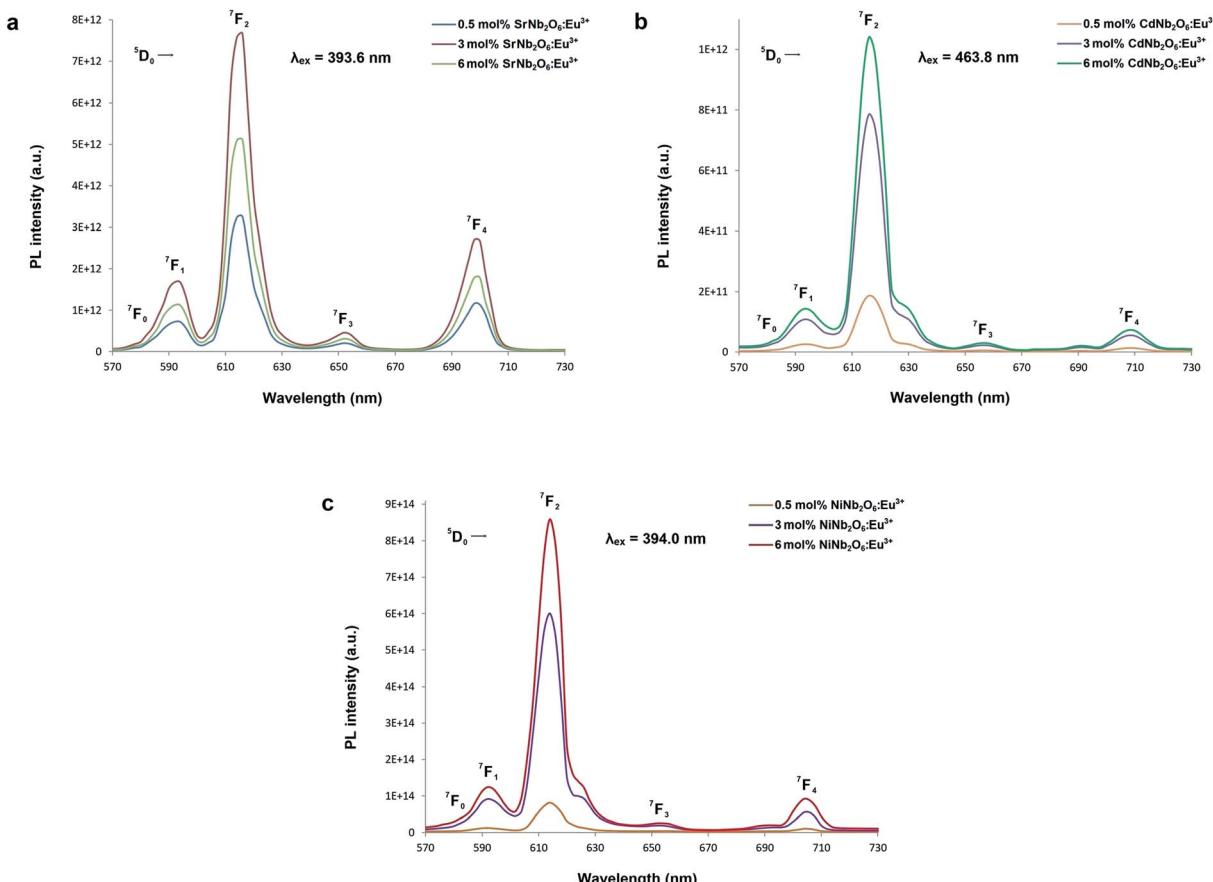


Fig. 6 PL emission spectra of the phosphors: (a)  $\text{SrNb}_2\text{O}_6:\text{Eu}^{3+}$ , (b)  $\text{CdNb}_2\text{O}_6:\text{Eu}^{3+}$ , and (c)  $\text{NiNb}_2\text{O}_6:\text{Eu}^{3+}$ .

$\rightarrow 7\text{F}_0$ ,  $5\text{D}_0 \rightarrow 7\text{F}_1$ ,  $5\text{D}_0 \rightarrow 7\text{F}_2$ ,  $5\text{D}_0 \rightarrow 7\text{F}_3$ ,  $5\text{D}_0 \rightarrow 7\text{F}_4$  transitions with the excitation of 393.6, 463.8, and 394.0 nm, respectively. The PL emissions of the  $\text{CdNb}_2\text{O}_6:\text{Eu}^{3+}$  and  $\text{NiNb}_2\text{O}_6:\text{Eu}^{3+}$  increased up to 6 mol%, while the  $\text{SrNb}_2\text{O}_6:\text{Eu}^{3+}$  emission decreased after 3 mol% due to the concentration quenching or nonradiative energy transfer, which originated from the host defects and the distance  $\text{RE}^{3+}-\text{RE}^{3+}$ .<sup>5,6</sup> In all the examples, the emission intensities of the  $5\text{D}_0 \rightarrow 7\text{F}_2$  (electric dipole) transition were higher than the  $5\text{D}_0 \rightarrow 7\text{F}_1$  (magnetic dipole) transition. This indicates that the  $\text{Eu}^{3+}$  ions occupied crystallographic sites without an inversion center.<sup>19,20</sup>

The radioluminescence (RL) emissions of  $\text{MNb}_2\text{O}_6:\text{Eu}^{3+}$  ( $\text{M} = \text{Sr, Cd, Ni}$ ) phosphors were monitored with the  $5\text{D}_0 \rightarrow 7\text{F}_0$ ,  $7\text{F}_1$ ,  $7\text{F}_2$ ,  $7\text{F}_3$ ,  $7\text{F}_4$  transitions under X-ray irradiation, as shown in Fig. 7(a-c). Also, the  $5\text{D}_0 \rightarrow 7\text{F}_5$  and  $5\text{D}_0 \rightarrow 7\text{F}_6$  transitions detected with RL are given in the inset figures in Fig. 7(a-c). The RL emissions of the phosphors showed a similarity as in the PL and decreased at 6 mol% of  $\text{SrNb}_2\text{O}_6:\text{Eu}^{3+}$ . Additionally, in the RL emissions of  $\text{SrNb}_2\text{O}_6:\text{Eu}^{3+}$ , an extra intensity increase or asymmetry ( $R$ ) increase occurred at the  $5\text{D}_0 \rightarrow 7\text{F}_2$  transition. Therefore both mechanisms could be compared based on the asymmetry, and the  $R$ -value variation of PL-RL emissions depending on the  $\text{Eu}^{3+}$  concentration is given Fig. 8. The  $R$ -values of  $\text{MNb}_2\text{O}_6:\text{Eu}^{3+}$  ( $\text{M} = \text{Sr, Cd, Ni}$ ) phosphors were found to be 4.38–4.44, 6.58–7.13, 5.68–6.78 for PL, and 6.56–7.15, 6.38–

7.42, 6.03–6.89 for RL, respectively. The  $R$ -value or ( $5\text{D}_0 \rightarrow 7\text{F}_2$ )/( $5\text{D}_0 \rightarrow 7\text{F}_1$ ) ratio can be used as an indicator to predict the symmetry of the local environment of  $\text{Eu}^{3+}$  ion; whereby a high  $R$ -value indicates an increase in  $\text{Eu}^{3+}-\text{O}^{2-}$  covalency and a low symmetry/more distorted environment.<sup>5</sup> As seen in Fig. 8, the  $R$ -values of the PL-RL mechanism for  $\text{CdNb}_2\text{O}_6:\text{Eu}^{3+}$  and  $\text{NiNb}_2\text{O}_6:\text{Eu}^{3+}$  were close to each other. However, the  $R$ -value of RL for  $\text{SrNb}_2\text{O}_6:\text{Eu}^{3+}$  was about 50% higher than the  $R$ -value of PL. The relatively low asymmetry of  $\text{SrNb}_2\text{O}_6:\text{Eu}^{3+}$  in PL increased in RL and reached levels close to other phosphors. Although the same basic transitions occur in PL and RL emissions, they do not contribute equally to the excitation mechanisms. X-ray irradiation of RL does not excite the CTB of the host but instead causes the formation of electron-hole pairs in its conduction and valence bands that recombine at the emission center, in which the energy is ultimately deposited.<sup>7,21</sup> X-ray irradiation can change the dipole moments and emission spectrum of  $\text{Eu}^{3+}$  in the host. Thus, although the symmetry of the  $\text{Eu}^{3+}$  local environment decreases to some extent with the high-energy photons of RL, the transformation will likely be temporary and the  $\text{Eu}^{3+}$  local environment symmetry will return to its initial state when X-ray irradiation is interrupted.<sup>7,21</sup>

The possible PL and RL mechanisms of  $\text{MNb}_2\text{O}_6:\text{Eu}^{3+}$  ( $\text{M} = \text{Sr, Cd, Ni}$ ) phosphors are schematically illustrated in Fig. 9(a and b), respectively. Fig. 9(a) shows the PL mechanism and indicates the possible pathways in the PL process. Excitation

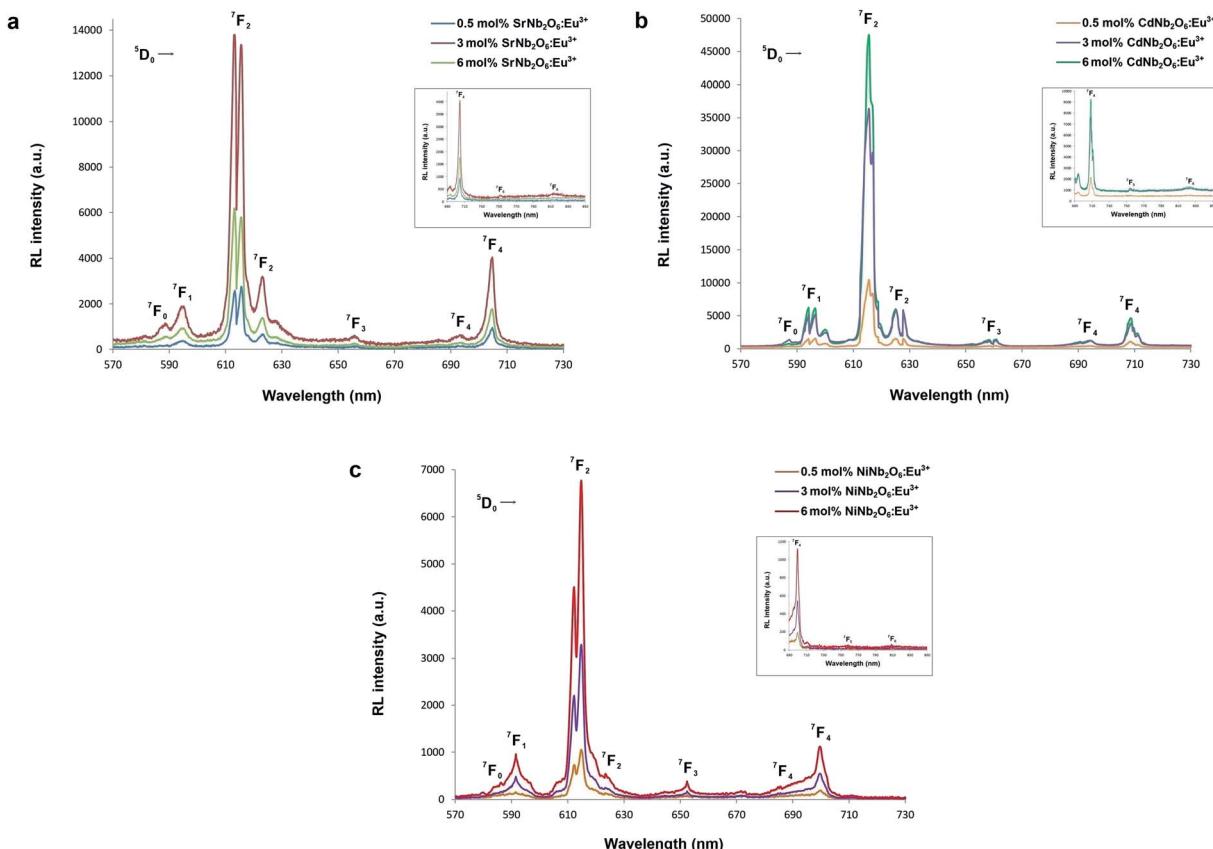


Fig. 7 RL emission spectra of the phosphors: (a)  $\text{SrNb}_2\text{O}_6:\text{Eu}^{3+}$ , (b)  $\text{CdNb}_2\text{O}_6:\text{Eu}^{3+}$ , and (c)  $\text{NiNb}_2\text{O}_6:\text{Eu}^{3+}$ . The  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$  ( $j = 0, 1, 2, 3, 4$ ) transitions between 570–730 nm, and (inset figures) the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$  ( $j = 5, 6$ ) transitions between 690–850 nm.

may consist of two processes, either by transferring the valence band electrons to the charge-transfer band (CTB) or by jumping to the higher levels of  $\text{Eu}^{3+}$ .<sup>6</sup> Excitation with charge transfer takes place at 276–278 nm while direct excitation of  $\text{Eu}^{3+}$  occurs at 393.6, 463.8, 394.0 nm. After excitation, the excited electrons come to the lowest excited level ( ${}^5\text{D}_0$ ) of  $\text{Eu}^{3+}$  by a nonradiative transition. Then it can make ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$ ) transitions to the lower

levels, in which emissions of  $\text{Eu}^{3+}$  would occur. The RL possible mechanism of  $\text{MNB}_2\text{O}_6:\text{Eu}^{3+}$  ( $\text{M} = \text{Sr, Cd, Ni}$ ) phosphors is presented in Fig. 9(b). The electrons of  $\text{Eu}^{3+}$  in the ground state ( ${}^7\text{F}_j$ ) promote the conduction band (CB), while the holes stay in the valence band (VB). X-ray induced electrons move in the CB and then part of them transfer to the excitation levels of  $\text{Eu}^{3+}$ . Also, the formation of traps is possible in the RL mechanism, and a part of the electrons can be captured by the traps, although this is not shown in the figure. Finally, when X-ray-induced electrons move to the ground state, they would be released at the appropriate energy level in which RL emissions take place with the recombination of the electrons and holes.

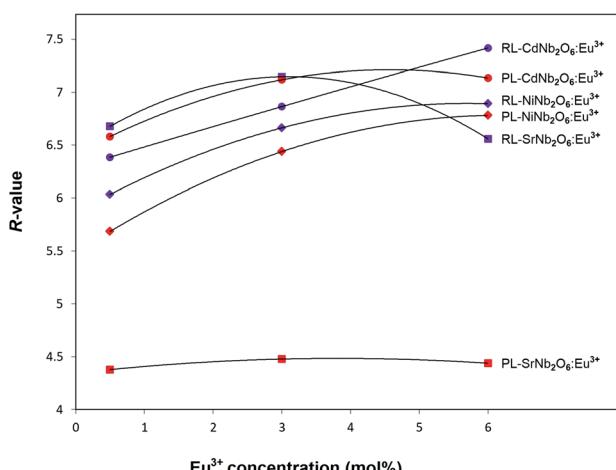


Fig. 8  $R$ -Value variation for PL and RL mechanisms depending on the  $\text{Eu}^{3+}$  concentration.

### 3.3. Judd–Ofelt analysis and radiative properties

Judd–Ofelt (JO) intensity parameters are critical to evaluate the performance of luminescent materials.<sup>22,23</sup> Among the  $\text{RE}^{3+}$  ions,  $\text{Eu}^{3+}$  has a unique feature for calculation of the JO intensity parameters due to the magnetic dipole transition ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ ) which is independent of the environment and can be used as a reference for transitions arising from the  ${}^5\text{D}_0$  level. Using the emission spectra for  $\text{Eu}^{3+}$ -doped materials, the JO intensity parameters  $\mathcal{Q}_J$  ( $J = 2, 4, 6$ ) can be calculated by eqn (1):<sup>24</sup>

$$\mathcal{Q}_J = \frac{S_{\text{MD}}(V_1^3)}{e^2(V_J^3)} \frac{9n^3}{n(n^2 + 2)^2} \frac{\int I_1(V_1)}{|\langle J \parallel U^J \parallel J' \rangle|^2 \int I_L(V_J)} \quad (1)$$



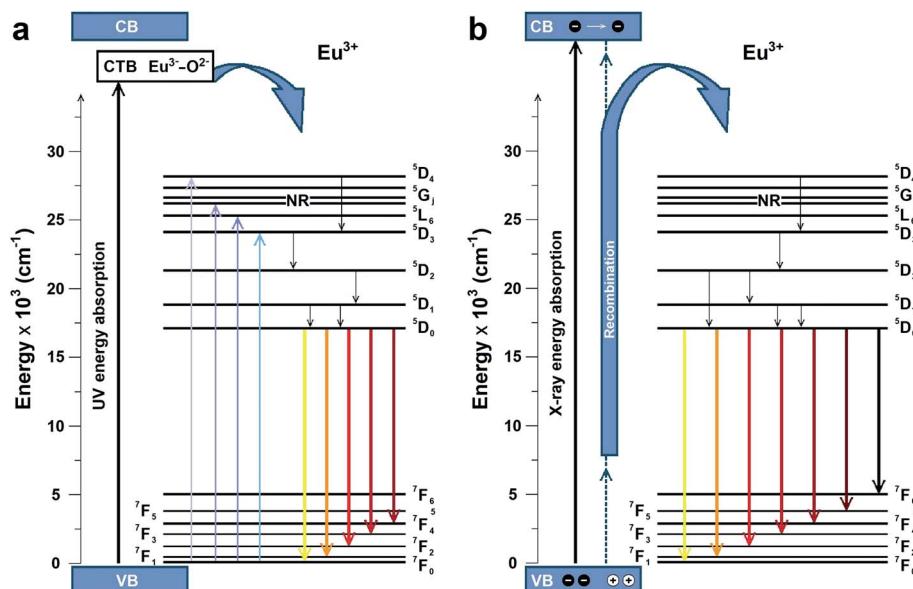


Fig. 9 Schematic energy level diagram to illustrate the possible (a) PL and (b) RL mechanisms.

where  $V_1$ ,  $V_J$  and  $I_1$ ,  $I_J$  are the frequencies and integrated intensities of the  $^7F_1$  and  $^7F_J$  ( $J = 2, 4, 6$ ) transitions respectively,  $e = 4.803 \times 10^{-10}$  esu (1 esu =  $N^{-5/2}$  cm =  $gr^{1/2}$  cm $^{3/2}$  s $^{-1}$ ) is the elementary charge,  $n$  is the refractive index,  $S_{MD} = 9.6 \times 10^{-42}$  esu $^2$  cm $^2$  is the line strength of the magnetic dipole, which was taken from ref. 24, and  $|\langle J||U^J||J' \rangle|^2$  represent the double-reduced matrix elements of the unit tensor operators, which are independent of the local environment of the ion. All the reduced matrix elements ( $|\langle J||U^J||J' \rangle|^2$ ) for electric-dipole (ED) transitions arising from the  $^5D_0$  level are zero, except for the levels  $^7F_J$ , (where  $J = 2, 4, 6$ )  $U^2 = 0.0032$ ,  $U^4 = 0.0023$ , and  $U^6 = 0.0002$ .<sup>24</sup> The  $^5D_0 \rightarrow ^7F_J$  ( $J = 1, 2, 4, 6$ ) transitions are used in the calculation of the JO parameters for the radiative transition probability. However, the  $^5D_0 \rightarrow ^7F_J$  ( $J = 0, 3, 5$ ) transitions are forbidden and are not included in the determination of the transition probabilities.<sup>24</sup> According to Judd–Ofelt theory, the spontaneous transition probability ( $A$ ) is related to its magnetic dipole strength ( $S_{MD}$ ) and electric-dipole strength ( $S_{ED}$ ), which can be calculated by eqn (2):<sup>22,23</sup>

$$A(J, J') = \frac{64\pi^4 V^3}{3h(2J+1)} [\chi_{ED} S_{ED} + \chi_{MD} S_{MD}] \quad (2)$$

where  $J$  is the total angular momentum of the initial state, and  $h$  is Planck's constant. The electric-dipole line strengths ( $S_{ED}$ ) can be calculated from the JO parameters by eqn (3):<sup>7</sup>

$$S_{ED}(J, J') = e^2 \sum_{J=2,4,6} \mathcal{Q}_J |\langle J||U^J||J' \rangle|^2 \quad (3)$$

where  $|\langle J||U^J||J' \rangle|^2$  is the symbol of the squared reduced matrix elements, and  $\chi_{ED}$  and  $\chi_{MD}$  are the local field corrections for the ED and MD transitions, which can be found by eqn (4) and (5), respectively:

$$\chi_{ED} = \frac{n(n^2 + 2)^2}{9} \quad (4)$$

$$\chi_{MD} = n^3 \quad (5)$$

where  $n$  is the refractive index. The  $n = 1.854$  value for  $\text{SrNb}_2\text{O}_6$  was taken from ref. 7. The  $n$  value for  $\text{CdNb}_2\text{O}_6$  and  $\text{NiNb}_2\text{O}_6$  can be estimated from the Lorenz–Lorentz formula eqn (6):<sup>25–29</sup>

$$\frac{n^2 - 1}{n^2 + 2} \frac{1}{\rho} = \frac{\sum l_i r_i}{M} \quad (6)$$

where  $M$  is the molar mass of the compound,  $l_i$  is the atomic number of the element in the nominal chemical formula of the compound,  $\rho$  is the density, and  $r_i$  is the specific refraction of the compound. The refraction index ( $n$ ) values for  $\text{CdNb}_2\text{O}_6$  and  $\text{NiNb}_2\text{O}_6$  were determined as 1.958 and 2.003, respectively.

The spectral results of the phosphors, JO intensity parameters ( $\mathcal{Q}_2$ ,  $\mathcal{Q}_4$ ), radiative transition probabilities ( $A(J, J')$ ), and total radiative transition probabilities ( $\sum A(J, J')$  or  $A_t$ ) are given in Table 1. The  $\mathcal{Q}_2$  parameter shows the short-range effects, while the  $\mathcal{Q}_4$  parameter shows the long-range effects.<sup>25,31</sup> The effects of the  $\mathcal{Q}_2$  parameter are short-range and are associated with the covalence and environmental changes of the  $\text{Eu}^{3+}$  ion symmetry.<sup>19,20</sup> The high value of  $\mathcal{Q}_2$  or the trend  $\mathcal{Q}_2 > \mathcal{Q}_4$  is evaluated to show the high covalence of the  $\text{Eu}^{3+}$ – $\text{O}^{2-}$  bond character (ionic or covalent) and the high asymmetry or distortion of the local symmetry of  $\text{Eu}^{3+}$  sites.<sup>7,31</sup> Accordingly, a high  $\mathcal{Q}_2$  parameter or  $\mathcal{Q}_2 > \mathcal{Q}_4$  tendency for all the phosphors can be attributed to the low symmetry  $\text{Eu}^{3+}$  ion and the more covalent or less ionic character of the  $\text{Eu}^{3+}$ – $\text{O}^{2-}$  bond. On the other hand, the effects of the  $\mathcal{Q}_4$  parameter are long-range and are not directly related to the symmetry of the  $\text{Eu}^{3+}$  ion, but the electron density on the surrounding ligands.<sup>30,31</sup> In all phosphors, the parameter of  $\mathcal{Q}_4$  decreased with increasing  $\text{Eu}^{3+}$  concentration, which indicated an increase in electron density in the ligands.

The branching ratio ( $\beta$  or  $\beta_{cal}$ ) of the Judd–Ofelt theory can be found from the radiative transition probability ( $A(J, J')$ ) and total radiative transition probability  $\sum(A(J, J'))$  by eqn (7):<sup>7</sup>



**Table 1** J–O parameters ( $\Omega_2$ ,  $\Omega_4$ ), radiative transition and total transition probabilities ( $A(J, J')$ ,  $A_r$ ), branching ratios ( $\beta_{cal}$ ), ( $\beta_{exp}$ )), and branching ratio differences (%) of the  $MNb_2O_6$ :Eu<sup>3+</sup> ( $M$  = Sr, Cd, Ni) phosphors

| Phosphor   | Eu <sup>3+</sup> conc. (mol%) | Eu <sup>3+</sup> transitions | $\Omega_2$ ( $10^{-20}$ cm $^2$ ) | $\Omega_4$ ( $10^{-20}$ cm $^2$ ) | $A(J, J')$ (s $^{-1}$ ) | $A_r$ (s $^{-1}$ ) | $\beta_{cal}$ (%) | $\beta_{exp}$ (%) | Difference (%) |
|--|-------------------------------|------------------------------|-----------------------------------|-----------------------------------|-------------------------|--------------------|-------------------|-------------------|----------------|
| SrNb <sub>2</sub> O <sub>6</sub> :Eu <sup>3+</sup> | 0.5                           | $^5D_0 \rightarrow ^7F_1$    | 7.148                             | 5.837                             | 92.101                  | 694.935            | 13.25             | 14.13             | 6.20           |
|  |                               | $^5D_0 \rightarrow ^7F_2$    |                                   |                                   | 429.055                 |                    | 61.74             | 63.24             | 2.37           |
|  |                               | $^5D_0 \rightarrow ^7F_4$    |                                   |                                   | 173.779                 |                    | 25.01             | 22.63             | 9.49           |
|  | 3                             | $^5D_0 \rightarrow ^7F_1$    | 7.209                             | 5.818                             | 92.026                  | 697.946            | 13.19             | 14.05             | 6.16           |
|  |                               | $^5D_0 \rightarrow ^7F_2$    |                                   |                                   | 432.719                 |                    | 61.99             | 63.49             | 2.35           |
|  |                               | $^5D_0 \rightarrow ^7F_4$    |                                   |                                   | 173.201                 |                    | 24.82             | 22.46             | 9.50           |
|  | 6                             | $^5D_0 \rightarrow ^7F_1$    | 7.172                             | 5.779                             | 92.194                  | 694.717            | 13.27             | 14.15             | 6.80           |
|  |                               | $^5D_0 \rightarrow ^7F_2$    |                                   |                                   | 430.474                 |                    | 61.96             | 63.44             | 2.33           |
|  |                               | $^5D_0 \rightarrow ^7F_4$    |                                   |                                   | 172.049                 |                    | 24.77             | 22.41             | 9.52           |
| CdNb <sub>2</sub> O <sub>6</sub> :Eu <sup>3+</sup> | 0.5                           | $^5D_0 \rightarrow ^7F_1$    | 7.360                             | 1.513                             | 107.954                 | 699.085            | 15.44             | 16.09             | 4.04           |
|  |                               | $^5D_0 \rightarrow ^7F_2$    |                                   |                                   | 538.924                 |                    | 77.09             | 77.40             | 0.39           |
|  |                               | $^5D_0 \rightarrow ^7F_4$    |                                   |                                   | 52.207                  |                    | 7.47              | 6.51              | 12.78          |
|  | 3                             | $^5D_0 \rightarrow ^7F_1$    | 7.788                             | 1.396                             | 107.933                 | 726.332            | 14.86             | 15.47             | 3.95           |
|  |                               | $^5D_0 \rightarrow ^7F_2$    |                                   |                                   | 570.238                 |                    | 78.51             | 78.75             | 0.31           |
|  |                               | $^5D_0 \rightarrow ^7F_4$    |                                   |                                   | 48.161                  |                    | 6.63              | 5.78              | 12.86          |
|  | 6                             | $^5D_0 \rightarrow ^7F_1$    | 7.852                             | 1.388                             | 107.916                 | 730.720            | 14.77             | 15.37             | 3.94           |
|  |                               | $^5D_0 \rightarrow ^7F_2$    |                                   |                                   | 574.902                 |                    | 78.67             | 78.92             | 0.30           |
|  |                               | $^5D_0 \rightarrow ^7F_4$    |                                   |                                   | 47.902                  |                    | 6.56              | 5.71              | 12.86          |
| NiNb <sub>2</sub> O <sub>6</sub> :Eu <sup>3+</sup> | 0.5                           | $^5D_0 \rightarrow ^7F_1$    | 8.529                             | 3.235                             | 116.395                 | 926.132            | 12.57             | 13.19             | 4.75           |
|  |                               | $^5D_0 \rightarrow ^7F_2$    |                                   |                                   | 685.886                 |                    | 74.06             | 75.00             | 1.25           |
|  |                               | $^5D_0 \rightarrow ^7F_4$    |                                   |                                   | 123.851                 |                    | 13.37             | 11.81             | 11.72          |
|  | 3                             | $^5D_0 \rightarrow ^7F_1$    | 9.658                             | 2.270                             | 116.375                 | 979.958            | 11.88             | 12.40             | 4.21           |
|  |                               | $^5D_0 \rightarrow ^7F_2$    |                                   |                                   | 776.661                 |                    | 79.25             | 79.82             | 0.70           |
|  |                               | $^5D_0 \rightarrow ^7F_4$    |                                   |                                   | 86.922                  |                    | 8.87              | 7.79              | 12.21          |
|  | 6                             | $^5D_0 \rightarrow ^7F_1$    | 10.023                            | 2.726                             | 116.340                 | 1043.388           | 11.15             | 11.66             | 4.37           |
|  |                               | $^5D_0 \rightarrow ^7F_2$    |                                   |                                   | 822.662                 |                    | 78.85             | 79.54             | 0.88           |
|  |                               | $^5D_0 \rightarrow ^7F_4$    |                                   |                                   | 104.386                 |                    | 10.00             | 8.80              | 12.06          |

$$\beta(\%) = \frac{A(J, J')}{\sum A(J, J')} \times 100\% \quad (7)$$

The branching ratios ( $\beta_{cal}$ ) of  $^5D_0 \rightarrow ^7F_2$  transition for CdNb<sub>2</sub>O<sub>6</sub>:Eu<sup>3+</sup> and NiNb<sub>2</sub>O<sub>6</sub>:Eu<sup>3+</sup> were found as 77.09–78.67% and 74.06–79.25%, respectively. The SrNb<sub>2</sub>O<sub>6</sub>:Eu<sup>3+</sup> had a relatively low branching ratio ranging from 61.74–61.99%, for which the results are given in Table 1. The  $\beta_{cal}$  values of the  $^5D_0 \rightarrow ^7F_2$  transition for all phosphors were over 60%. The high value of branching ratio ( $\beta > 50$ ) indicated a potential laser emission.<sup>7,24</sup> The branching ratios ( $\beta_{cal}$ ) of the Judd–Ofelt theory can be evaluated using experimental branching ratios ( $\beta_{exp}$ ), which can be obtained directly from the emission spectrum. On the other hand, the intrinsic error of the Judd–Ofelt theory in describing spectral intensities is usually about 15%.<sup>7,32</sup> Accordingly, differences between the experimental ( $\beta_{exp}$ ) and calculated values ( $\beta_{cal}$ ) for all samples occurred between 0.3–12.86%, and they were all below 15% (Table 1).

In the Judd–Ofelt calculation, the  $\Omega_2$  and  $\Omega_4$  parameters were used, but the  $\Omega_6$  parameter was not included since the  $^5D_0 \rightarrow ^7F_6$  transition remaining in the infrared region could not be detected by PL. Similar studies have been reported using the  $\Omega_2$  and  $\Omega_4$  parameters for JO calculations.<sup>24,30</sup> The  $^5D_0 \rightarrow ^7F_6$  transition outside the visible spectrum is very weak in many materials.<sup>24</sup> In this study, the weak intensity of the  $^5D_0 \rightarrow ^7F_6$  transition detected by RL in Fig. 7(a–c) supports this situation.

Based on the  $^5D_0 \rightarrow ^7F_6$  transition observed by RL, the  $\Omega_6$  parameters were determined for the samples with the highest emissions intensity. The  $\Omega_6$  parameters and total radiative transition probabilities ( $\sum A(J, J')$  or  $A_r$ ) of the  $^5D_0 \rightarrow ^7F_6$  transition were estimated as  $2.226 \times 10^{-20}$ ,  $1.103 \times 10^{-20}$ ,  $0.155 \times 10^{-20}$  cm $^2$ , and  $3.636$ ,  $2.116$ ,  $0.341$  s $^{-1}$  for 3 mol% (SrNb<sub>2</sub>O<sub>6</sub>:Eu<sup>3+</sup>), 6 mol% (CdNb<sub>2</sub>O<sub>6</sub>:Eu<sup>3+</sup>), 6 mol% (NiNb<sub>2</sub>O<sub>6</sub>:Eu<sup>3+</sup>), respectively. The branching ratios ( $\beta_{cal}$ ) of the  $^5D_0 \rightarrow ^7F_6$  transition (or the ratio of the  $^5D_0 \rightarrow ^7F_6$  transition probability to the total radiative transition probability) were found in the range of 0.03–0.52%. Also, the branching ratios ( $\beta_{exp}$ ) of the  $^5D_0 \rightarrow ^7F_6$  transition from the emission spectra were between 0.18–0.40%. Accordingly, based on the determination of the branching ratios using the RL spectra, the effect of the  $^5D_0 \rightarrow ^7F_6$  transition on the quantum efficiency or other radiative parameters was negligibly minimal, and its exclusion will not have a significant effect.

Fig. 10(a–c) show the decay curves of MNb<sub>2</sub>O<sub>6</sub>:Eu<sup>3+</sup> ( $M$  = Sr, Cd, Ni) phosphors for  $^5D_0 \rightarrow ^7F_2$  transitions ( $\lambda_{em} = 615.7$ , 616.2, 614.0 nm) recorded with excitations at 393.6, 463.8, and 394.0 nm, respectively. The observed lifetime or average decay ( $\tau$ ) curves can be established by the following two-time temporal dependence in eqn (8):<sup>6</sup>

$$I_{(t)}^L = I_{(0)}^L + B_1 \exp \frac{t_0 - t}{\tau_1} + B_2 \exp \frac{t_0 - t}{\tau_2} \quad (8)$$

where the luminescence intensities are  $I_{(t)}^L$  and  $I_{(0)}^L$ , the fitting constants are  $B_1$  and  $B_2$ , and the short and long lifetimes for the

exponential components are  $\tau_1$  and  $\tau_2$  respectively. The average (observed) lifetime ( $\tau$ ) can be calculated through eqn (9) according to the variables in eqn (8):<sup>6</sup>

$$\tau = \frac{B_1 \tau_1^2 + B_2 \tau_2^2}{B_1 \tau_1 + B_2 \tau_2} \quad (9)$$

The observed lifetimes ( $\tau$ ) of the  $\text{MNB}_2\text{O}_6:\text{Eu}^{3+}$  ( $\text{M} = \text{Sr, Cd, Ni}$ ) phosphors for the  ${}^5\text{D}_0$  level varied from 914.36, 673.35, 119.08 to 828.69, 573.29, 113.75  $\mu\text{s}$ , respectively (Table 2). The observed lifetime ( $\tau$ ) represents the sum of nonradiative ( $\tau_{\text{nr}}$ ) and the radiative ( $\tau_{\text{r}}$ ) lifetimes, which are expressed by eqn (10). The value of the radiative (experimental) lifetime ( $\tau_{\text{r}}$ ) can be determined from the total radiative transition probability ( $A_{\text{r}}$ ) by eqn (11):

$$\tau = \tau_{\text{r}} + \tau_{\text{nr}} \quad (10)$$

$$\tau_{\text{r}} = \frac{1}{A_{\text{r}}} \quad (11)$$

The radiative lifetime can also be found theoretically by direct calculation from eqn (12), which is related to the emission spectrum of  $\text{Eu}^{3+}$ .<sup>24,32</sup>

$$\tau_{\text{th}} = \frac{n_1^3}{14.65} \frac{I_1}{I_{\text{tot}}} \quad (12)$$

where  $\tau_{\text{th}}$  is the theoretical radiative lifetime,  $I_1$  is the integrated intensity of the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  transition,  $I_{\text{tot}}$  is the total integrated intensity, and  $n$  is the refractive index. The quantum efficiency ( $\eta_{\text{QE}}$ ) of a phosphor can be defined by the ratio of the number of photons emitted (observed lifetime:  $\tau$ ) to the number of photons absorbed (radiative lifetimes:  $\tau_{\text{r}}$ ). Accordingly, the quantum efficiency ( $\eta_{\text{QE}}$ ) and theoretical quantum efficiency ( $\eta_{\text{QE}}^{\text{th}}$ ) can be determined by eqn (13) and (14), respectively:

$$\eta_{\text{QE}} = \frac{\tau}{\tau_{\text{r}}} \quad (13)$$

$$\eta_{\text{QE}}^{\text{th}} = \frac{\tau}{\tau_{\text{th}}} \quad (14)$$

A comparison of the radiative lifetimes ( $\tau_{\text{r}}, \tau_{\text{th}}$ ) and quantum efficiencies ( $\eta_{\text{QE}}, \eta_{\text{QE}}^{\text{th}}$ ) of  $\text{MNB}_2\text{O}_6:\text{Eu}^{3+}$  ( $\text{M} = \text{Sr, Cd, Ni}$ ) phosphors was performed and the results are given in Table 2. The  $\eta_{\text{QE}}\%$  values for the  $\text{SnNB}_2\text{O}_6:\text{Eu}^{3+}$  and  $\text{CdNB}_2\text{O}_6:\text{Eu}^{3+}$  were estimated as follows: 57.57–63.54% and 41.89–47.07%, respectively. However, the  $\eta_{\text{QE}}\%$  value of  $\text{NiNB}_2\text{O}_6:\text{Eu}^{3+}$  showed a low efficiency and varied between 11.22–11.88%. The differences of the  $\eta_{\text{QE}}\%$  (calculated-JO) and  $\eta_{\text{QE}}^{\text{th}}$  (theoretical) for  $\text{SnNB}_2\text{O}_6:\text{Eu}^{3+}$  varied between 0.41–0.69%, whereas the compatibility of the efficiencies for  $\text{CdNB}_2\text{O}_6:\text{Eu}^{3+}$  and  $\text{NiNB}_2\text{O}_6:\text{Eu}^{3+}$  decreased somewhat and the difference varied between 4.83–5.99 and 2.92–7.16, respectively (Table 2).

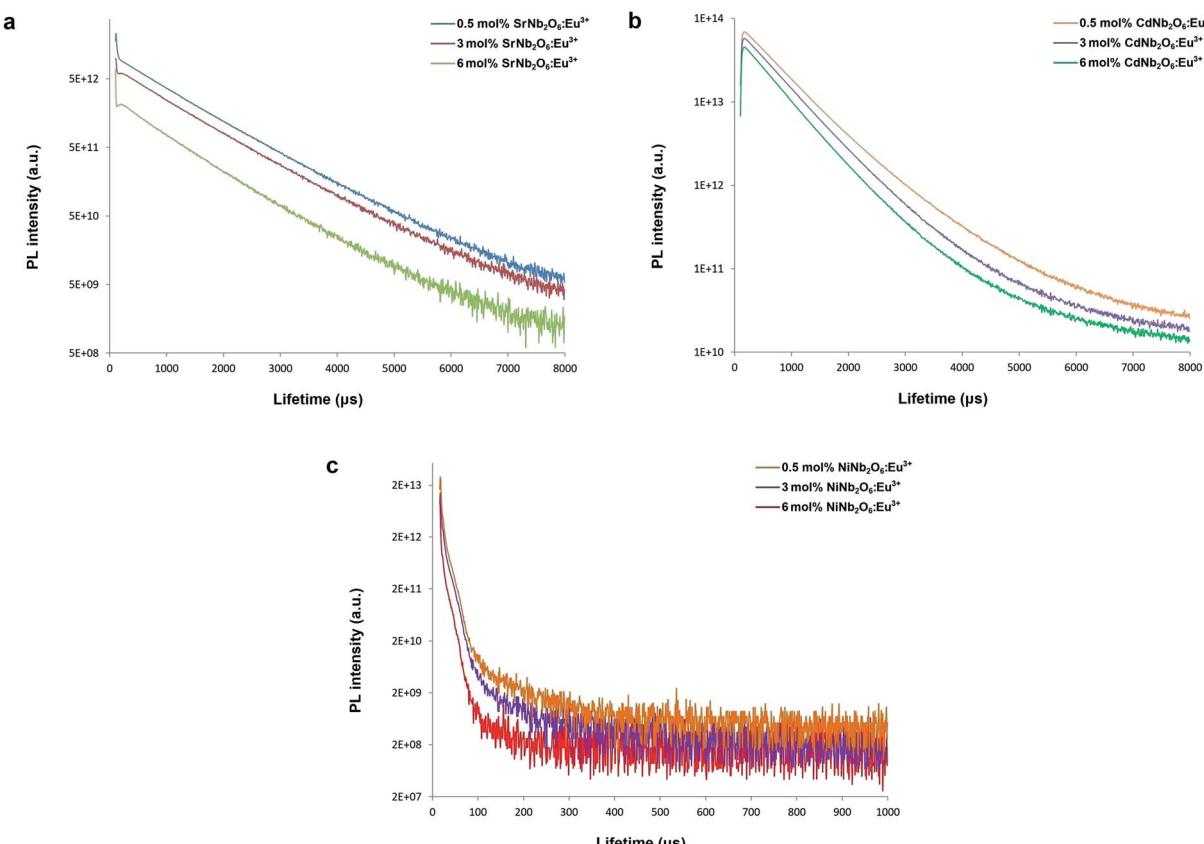


Fig. 10 PL lifetime curves for  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition of the phosphors: (a)  $\text{SrNB}_2\text{O}_6:\text{Eu}^{3+}$ , (b)  $\text{CdNB}_2\text{O}_6:\text{Eu}^{3+}$ , and (c)  $\text{NiNB}_2\text{O}_6:\text{Eu}^{3+}$ .



**Table 2** The radiative lifetimes ( $\tau_r$ ), theoretical radiative lifetimes ( $\tau_{th}$ ), observed lifetimes ( $\tau$ ), quantum efficiencies ( $\eta_{QE}$ ), theoretical quantum efficiencies ( $\eta_{QE}^{th}$ ), and quantum efficiency differences (%) of the  $MNb_2O_6:Eu^{3+}$  ( $M = Sr, Cd, Ni$ ) phosphors

| Phosphor            | Eu <sup>3+</sup> conc. (mol%) | $\tau_r$ (μs) | $\tau_{th}$ (μs) | $\tau$ (μs) | $\eta_{QE}$ (%) | $\eta_{QE}^{th}$ (%) | Difference (%) |
|---------------------|-------------------------------|---------------|------------------|-------------|-----------------|----------------------|----------------|
| $SrNb_2O_6:Eu^{3+}$ | 0.5                           | 1438.98       | 1429.07          | 914.36      | 63.54           | 63.98                | 0.69           |
|                     | 3                             | 1432.78       | 1426.16          | 886.52      | 61.87           | 62.16                | 0.46           |
|                     | 6                             | 1439.43       | 1433.49          | 828.69      | 57.57           | 57.81                | 0.41           |
| $CdNb_2O_6:Eu^{3+}$ | 0.5                           | 1430.44       | 1344.79          | 673.35      | 47.07           | 50.07                | 5.99           |
|                     | 3                             | 1376.78       | 1308.06          | 609.02      | 44.24           | 46.56                | 4.99           |
|                     | 6                             | 1368.51       | 1302.47          | 573.29      | 41.89           | 44.02                | 4.83           |
| $NiNb_2O_6:Eu^{3+}$ | 0.5                           | 1080.76       | 1002.41          | 119.08      | 11.03           | 11.88                | 7.16           |
|                     | 3                             | 1020.45       | 989.21           | 115.91      | 11.36           | 11.72                | 3.06           |
|                     | 6                             | 958.42        | 930.47           | 113.75      | 11.87           | 12.22                | 2.92           |

The stimulated emission cross-section ( $\sigma_e$ ) is an important factor to predict the laser performance of a material. The stimulated emission cross-section ( $\sigma_e$ ) between the states  $J$  and  $J'$  having a probability of  $A(J, J')$  is given by eqn (15):<sup>7,20</sup>

$$\sigma_e(\lambda_p)(J, J') = \left[ \frac{(\lambda_p)^4}{8\pi cn^2 \Delta\lambda_{eff}} \right] A(J, J') \quad (15)$$

where  $c$  is the velocity of light,  $\lambda_p$  is the emission peak wavelength,  $\Delta\lambda_{eff}$  is the effective bandwidth of the emission transition and  $n$  is the refractive index of the matrix. The stimulated emission cross-section ( $\sigma_e$ ), gain bandwidth ( $\sigma_e \times \Delta\lambda_{eff}$ ), the effective bandwidth of emission transition ( $\Delta\lambda_{eff}$ ), and the optical gain ( $\sigma_e \times \tau$ ) results are given in Table 3. The large  $\sigma_e$

value for the potential laser performance at room temperature is an attractive feature for low threshold and high gain laser applications.<sup>7</sup> The  $\sigma_e$  parameters of the  $MNb_2O_6:Eu^{3+}$  ( $M = Sr, Cd, Ni$ ) phosphors were found as  $^7F_2 > ^7F_4 > ^7F_1$ . The product of the  $\sigma_e$  and  $\Delta\lambda_{eff}$  is another important parameter and helps predict the gain bandwidth ( $\sigma_e \times \Delta\lambda_{eff}$ ) of the optical amplifier. The high values of the product are better for the performance of the amplifier.<sup>7</sup> The gain bandwidths ( $\sigma_e \times \Delta\lambda_{eff}$ ) of the  $MNb_2O_6:Eu^{3+}$  ( $M = Sr, Cd, Ni$ ) phosphors with the highest emission were determined as follows:  $24.182 \times 10^{-28}$ ,  $28.674 \times 10^{-28}$ , and  $38.647 \times 10^{-28} \text{ cm}^3$ , respectively, corresponding to  $^5D_0 \rightarrow ^7F_2$  transition. The product of the  $\sigma_e$  and observed lifetime ( $\tau$ ) is an important consideration for high optical amplifier gain.<sup>7,33</sup>

**Table 3** The effective bandwidth of the emission transitions ( $\Delta\lambda_{eff}$ ), stimulated emission cross-sections ( $\sigma_e$ ), gain bandwidths ( $\sigma_e \times \Delta\lambda_{eff}$ ), and optical gains ( $\sigma_e \times \tau$ ) of the  $MNb_2O_6:Eu^{3+}$  ( $M = Sr, Cd, Ni$ ) phosphors

| Phosphor            | Eu <sup>3+</sup> conc. (mol%) | Eu <sup>3+</sup> transitions | $\Delta\lambda_{eff}$ (nm) | $\sigma_e (\times 10^{-22} \text{ cm}^2)$ | $\sigma_e \times \Delta\lambda_{eff} (\times 10^{-28} \text{ cm}^3)$ | $\sigma_e \times \tau (\times 10^{-25} \text{ cm}^2 \text{ s})$ |
|---------------------|-------------------------------|------------------------------|----------------------------|---|--|---|
| $SrNb_2O_6:Eu^{3+}$ | 0.5                           | $^5D_0 \rightarrow ^7F_1$    | 12.10                      | 3.627                                     | 4.388  |   |
|                     |                               | $^5D_0 \rightarrow ^7F_2$    | 10.08                      | 23.788                                    | 23.977   | 21.750  |
|                     |                               | $^5D_0 \rightarrow ^7F_4$    | 11.03                      | 14.452                                    | 15.933   |   |
|                     |                               | $^5D_0 \rightarrow ^7F_1$    | 12.15                      | 3.613                                     | 4.389  |   |
|                     |                               | $^5D_0 \rightarrow ^7F_2$    | 10.49                      | 23.057                                    | 24.182   |   |
|                     | 3                             | $^5D_0 \rightarrow ^7F_4$    | 11.21                      | 14.161                                    | 15.880   |   |
|                     |                               | $^5D_0 \rightarrow ^7F_1$    | 12.12                      | 3.618                                     | 4.387  |   |
|                     |                               | $^5D_0 \rightarrow ^7F_2$    | 10.34                      | 23.269                                    | 24.056   | 19.283  |
|                     |                               | $^5D_0 \rightarrow ^7F_4$    | 11.13                      | 14.168                                    | 15.775   |   |
|                     |                               | $^5D_0 \rightarrow ^7F_1$    | 14.36                      | 3.233                                     | 4.641  |   |
| $CdNb_2O_6:Eu^{3+}$ | 0.5                           | $^5D_0 \rightarrow ^7F_2$    | 11.41                      | 23.552                                    | 26.880   | 15.859  |
|                     |                               | $^5D_0 \rightarrow ^7F_4$    | 12.42                      | 3.683                                     | 4.574  |   |
|                     |                               | $^5D_0 \rightarrow ^7F_1$    | 15.19                      | 3.055                                     | 4.642  |   |
|                     |                               | $^5D_0 \rightarrow ^7F_2$    | 11.50                      | 24.727                                    | 28.442   | 15.059  |
|                     |                               | $^5D_0 \rightarrow ^7F_4$    | 12.80                      | 3.297                                     | 4.219  |   |
|                     | 3                             | $^5D_0 \rightarrow ^7F_1$    | 15.85                      | 2.929                                     | 4.643  |   |
|                     |                               | $^5D_0 \rightarrow ^7F_2$    | 11.92                      | 24.055                                    | 28.674   | 13.790  |
|                     |                               | $^5D_0 \rightarrow ^7F_4$    | 12.91                      | 3.251                                     | 4.197  |   |
|                     |                               | $^5D_0 \rightarrow ^7F_1$    | 12.96                      | 3.657                                     | 4.737  |   |
|                     |                               | $^5D_0 \rightarrow ^7F_2$    | 10.91                      | 29.546                                    | 32.222   |   |
| $NiNb_2O_6:Eu^{3+}$ | 0.5                           | $^5D_0 \rightarrow ^7F_4$    | 9.11                       | 11.060                                    | 10.081   | 3.518   |
|                     |                               | $^5D_0 \rightarrow ^7F_1$    | 13.39                      | 3.537                                     | 4.737  |   |
|                     |                               | $^5D_0 \rightarrow ^7F_2$    | 10.90                      | 33.487                                    | 36.486   | 3.881   |
|                     |                               | $^5D_0 \rightarrow ^7F_4$    | 9.63                       | 7.345                                     | 7.075  |   |
|                     |                               | $^5D_0 \rightarrow ^7F_1$    | 13.49                      | 3.512                                     | 4.738  |   |
|                     | 3                             | $^5D_0 \rightarrow ^7F_2$    | 11.03                      | 35.054                                    | 38.647   | 3.987   |
|                     |                               | $^5D_0 \rightarrow ^7F_4$    | 10.93                      | 7.777                                     | 8.497  |   |



The optical gains ( $\sigma_e \times \tau$ ) of  $\text{MNb}_2\text{O}_6:\text{Eu}^{3+}$  ( $\text{M} = \text{Sr, Cd, Ni}$ ) varied between  $19.283\text{--}21.750 \times 10^{-25}$ ,  $13.790\text{--}15.859 \times 10^{-25}$ , and  $3.518\text{--}3.987 \times 10^{-25} \text{ cm}^2 \text{ s}$ , respectively. The large values of the stimulated emission cross-section, gain bandwidth, optical gain, and lifetime support that  $\text{MNb}_2\text{O}_6:\text{Eu}^{3+}$  ( $\text{M} = \text{Sr, Cd, Ni}$ ) phosphors can be helpful for the improvement of the red lasing and red color applications for display devices.

## 4. Conclusion

$\text{MNb}_2\text{O}_6:\text{Eu}^{3+}$  ( $\text{M} = \text{Sr, Cd, Ni}$ ) crystal powders synthesized by the molten salt method have an orthorhombic/monoclinic symmetry. SEM micrographs of  $\text{Eu}^{3+}$ -doped  $\text{SrNb}_2\text{O}_6$  exhibited characteristic nanorods for the grain structure, while the grain morphologies of  $\text{Eu}^{3+}$ -doped  $\text{CdNb}_2\text{O}_6$  and  $\text{NiNb}_2\text{O}_6$  differed in size and shape. The emissions of the phosphors were monitored in PL and RL with the  $^5\text{F}_0 \rightarrow ^7\text{F}_J$  ( $J = 0\text{--}4$ ) and  $^5\text{F}_0 \rightarrow ^7\text{F}_J$  ( $J = 0\text{--}6$ ) transitions of  $\text{Eu}^{3+}$ , respectively. The RL emissions of  $\text{SrNb}_2\text{O}_6:\text{Eu}^{3+}$  exhibited an extra increase at the  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  (electric dipole) transition, which was related to the decrease in local symmetry of  $\text{Eu}^{3+}$ ; however, this same effect was not seen for  $\text{CdNb}_2\text{O}_6:\text{Eu}^{3+}$  and  $\text{NiNb}_2\text{O}_6:\text{Eu}^{3+}$ . By determining the Judd-Ofelt intensity parameters ( $\Omega_2, \Omega_4$ ) from the emission spectrum, we calculated the radiative transition probabilities ( $A(J,J')$ ), branching ratios ( $\beta_{\text{cal}}$ ), and radiative lifetimes ( $\tau_r$ ). The branching ratio difference of the measured ( $\beta_{\text{exp}}$ ) from the emission spectrum and that calculated ( $\beta_{\text{cal}}$ ) from the JO parameters for all samples varied by 0.3–12.86%, which were all less than 15%. The high  $\Omega_2$  value or  $\Omega_2 > \Omega_4$  tendency for all the phosphors indicated the low symmetry  $\text{Eu}^{3+}$  ion and the more covalent character of the  $\text{Eu}^{3+}\text{--O}^{2-}$  bond. The order of quantum efficiencies ( $\eta_{\text{QE}}\%$ ) was found to be:  $\text{SrNb}_2\text{O}_6:\text{Eu}^{3+} > \text{CdNb}_2\text{O}_6:\text{Eu}^{3+} > \text{NiNb}_2\text{O}_6:\text{Eu}^{3+}$ . The quantum efficiencies ( $\eta_{\text{QE}}$ ) of the phosphors deviated slightly from the theoretically calculated quantum efficiencies ( $\eta_{\text{QE}}^{\text{th}}$ ). The bandwidths ( $\sigma_e \times \Delta\lambda_{\text{eff}}$ ) and optical gains ( $\sigma_e \times \tau$ ) were found to follow the trend:  $\text{SrNb}_2\text{O}_6:\text{Eu}^{3+} < \text{CdNb}_2\text{O}_6:\text{Eu}^{3+} < \text{NiNb}_2\text{O}_6:\text{Eu}^{3+}$  and  $\text{SrNb}_2\text{O}_6:\text{Eu}^{3+} > \text{CdNb}_2\text{O}_6:\text{Eu}^{3+} > \text{NiNb}_2\text{O}_6:\text{Eu}^{3+}$ , respectively. These results point out that  $\text{MNb}_2\text{O}_6:\text{Eu}^{3+}$  ( $\text{M} = \text{Sr, Cd, Ni}$ ) phosphors with strong emissions at  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition could be interesting candidates for RE-doped red phosphor applications and for future study.

## Conflicts of interest

There are no conflicts to declare.

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