Luminescence Properties of Lu$^{3+}$ doped Nd: YAG Transparent Ceramics

Wentao Jia$^{1,a}$, Qinlei Wei$^{2,b}$, Hongbo Zhang$^{1,e}$, Chunhui Su$^{1,d,*}$, Guozhong Ren$^{2,e}$, Mengjie Zhao$^{2,f}$

$^1$School of Material Science and Engineering, Changchun University of Science and Technology, Changchun 130022, China
$^2$Changchun Normal University, Changchun 130032, China
$^a$email: zhanghongbo@cust.edu.cn, $^b$email: 924547307@qq.com, $^e$email: zhb5388460@126.com, $^d$email: 4965594@qq.com, $^f$email: 472867406@qq.com
$^*Corresponding author: $^*email: sch@cust.edu.cn.

Abstract. Lu$_2$O$_3$ doped Nd: YAG transparent ceramics were prepared by solid-state reaction and vacuum sintering. Ionic size compensation was investigated by comparing the X-ray diffraction patterns (XRD) and Raman spectroscopy (Raman) of (Nd$_{0.06}$Lu$_{0.94}$)$_3$Al$_5$O$_{12}$ ceramics. The micrographs and element mappings of ceramics samples sintered at 1750°C for 50 h were analyzed by scanning electron microscope (SEM) and X-ray energy dispersive spectroscopy (EDS), respectively. The emission peak intensity of 1064 nm is the largest, which corresponds to the $4F_{3/2} \rightarrow 4I_{11/2}$ transition of Nd$^{3+}$. Fluorescence spectra and decay curves show that the fluorescence intensity was the highest when the concentration of Lu$_2$O$_3$ was 0.02, and the fluorescence lifetime was 193.92 µs. The elimination of lattice distortion is beneficial to the improvement of fluorescence properties, which can be attributed to ionic size compensation of Lu$^{3+}$.

1. Introduction
Nd: YAG transparent ceramics have caught wide attention in the solid-state laser material field due to its outstanding properties such as excellent luminescence properties, high hardness, and high-temperature resistance [1, 2]. High doping concentration and low cost of manufacturing make the Nd: YAG ceramics attractive with comparison to Nd: YAG single crystal [3, 4].

It is well-known that the Nd$^{3+}$ ions substitute the Y$^{3+}$ ions of the same charge state in the host lattice. However, the radii of the Nd$^{3+}$ ion (1.04Å) is larger than Y$^{3+}$(0.92Å), this substitution for Y$^{3+}$ increases the lattice distortion of YAG [5]. It leads to a reduction of the fluorescent lifetime due to the existence of lattice distortion [6]. In order to reduce lattice distortion, extra size compensation is required through doping small rare earth, such as Lu$^{3+}$ ion (0.86Å).

Within current research on Nd: YAG ceramic, Lu et al. reported that the Lu$^{3+}$ ions are doped into the YAG lattice can be relieved lattice distortion by co-precipitation method and vacuum sintering [7, 8]. Unfortunately, the fluorescence lifetime of transparent ceramics has been enhanced with the addition of Lu$^{3+}$, but the transmittance of ceramics has seriously decreased. Due to the extra doped Lu$^{3+}$ exceeds the original stoichiometric ratio of Nd: YAG, which cannot accurately eliminate lattice distortion. Besides, the co-precipitation method prolonged the experimental period of the transparent
ceramics and added complexity to the process when compared to the solid-state reaction method. Among these innovative matrices, \((\text{Nd}_{0.03}\text{Lu}_x\text{Y}_{2.97-x})_3\text{Al}_5\text{O}_{12}\) \((X=0.01\text{--}0.04)\) seems to be a good constitute because it requires a small amount of Lu\(^{3+}\). There is little difference between the concentration of the Lu\(_2\)O\(_3\) and Nd\(_2\)O\(_3\) in \((\text{Nd}_{0.03}\text{Lu}_x\text{Y}_{2.97-x})_3\text{Al}_5\text{O}_{12}\) \((X=0.01\text{--}0.04)\). We supposed that a similar effect would take place in Lu\(_2\)O\(_3\) doped \((\text{Nd}_{0.03}\text{Lu}_x\text{Y}_{2.97-x})_3\text{Al}_5\text{O}_{12}\) \((X=0.01\text{--}0.04)\) ceramics through solid-state reaction.

In this work, \((\text{Nd}_{0.06}\text{Lu}_x\text{Y}_{2.94-x})_3\text{Al}_5\text{O}_{12}\) would constitute a good combination to investigate ionic size compensation because it requires a small amount of Lu\(^{3+}\). The effect of Lu\(_2\)O\(_3\) on the structural, microstructures, and optical properties of Nd: YAG ceramics were studied using different characterization techniques.

2. Materials and Methods
High purity \(\text{Y}_2\text{O}_3\) \((99.999\%)\), \(\alpha-\text{Al}_2\text{O}_3\) \((99.99\%)\), \(\text{Lu}_2\text{O}_3\) \((99.99\%)\), \(\text{Nd}_2\text{O}_3\) \((99.99\%)\) powders were weighted with chemical compositions \((\text{Nd}_{0.06}\text{Lu}_x\text{Y}_{2.94-x})_3\text{Al}_5\text{O}_{12}\) \((X=0, 0.01, 0.02, 0.03, 0.04)\). The raw materials were poured into a high-purity \(\text{Al}_2\text{O}_3\) ball mill tank with ethanol using 0.5 wt% TEOS (Tetraethyl orthosilicate, \(>99.99\%\)) and 0.1wt%MgO (>99.99%) as the sintering aid. All slurries were uniformly mixed with a high-purity \(\text{ZrO}_2\) grinding ball and air-dried at 60°C for 2 h followed by sieving through a 200-mesh screen, after that, the mixture of the powders was calcined at 800°C for 4 h to eliminate organic residue. Green bodies with 19 mm in diameter and 2 mm in thickness were prepared from the powder mixtures under a uniaxial dry pressure of 10 MPa and a cold isostatic pressure of 300 MPa. After sintering the green bodies at 1750°C for 50h under vacuum \((1.0\times10^{-6}\text{ Pa})\), the obtained ceramics samples were annealed in air at 1450°C for 10h and mirror polished on both surfaces. These obtained \((\text{Nd}_{0.06}\text{Lu}_x\text{Y}_{2.94-x})_3\text{Al}_5\text{O}_{12}\) \((X=0, 0.01, 0.02, 0.03, 0.04)\) ceramics samples were named as S0, S1, S2, S3 and S4, respectively.

X-ray diffractometer (Rigaku 2500 PC, Japan) Cu-K\(\alpha_1\)target radiation \((\lambda=0.154\text{nm})\), the operating voltage is 40kV, the current is 30mA, the test angle \((\theta)\) is 20–80°. Raman spectra were measured by a T6400 micro-Raman spectrometer (RERU-YQ-006) with an excitation wavelength of 514.5 nm. The transmittance of the transparent ceramics was measured by a dual-beam UV-visible spectrophotometer (SHIMADZU, UV-1902). The SEM images and EDS spectra taken of samples were obtained by Using a SPI3800N scanning electron microscope (SEM, JEOL, JSM-7610F) operated at 10 kV. Fluorescence spectra and decay curves were measured on a spectrometer (Edinburgh Instruments FLS 980) with an 808-Laser (Opolette laser by Opotek) as the excitation source.

3. Results & Discussion
Figure 1(a) shows the change of the Nd: YAG crystal structure before and after doping with Lu\(^{3+}\) and the principle diagram of the elimination of lattice distortion, respectively. Fig. 1(b) shows the XRD patterns of different ceramics samples sintered at 1750°C for 50 h. The result shows that there were no impurity peaks were observed. The lattice constant increases first and then decreases with the increase of the Lu\(_2\)O\(_3\) doping content. When the doping amount of Lu\(_2\)O\(_3\) is 0.02, the lattice constant of the S2 sample is 12.010 Å, which is very close to the theoretical value 12.011 Å of the Nd: YAG single crystal [9, 10].
Figure 1. (a) Crystal structure of Lu$_2$O$_3$ doped Nd: YAG and schematic diagram of lattice distortion elimination, (b) XRD patterns, and (c) Raman spectra of ceramic samples sintered at 1750°C for 50 h.

Figure 1(c) shows the Raman spectra of different ceramics samples sintered at 1750°C for 50 h. The characteristic absorption peaks of YAG ceramics appeared at 260 cm$^{-1}$, 370 cm$^{-1}$, 402 cm$^{-1}$, 667 cm$^{-1}$, 690 cm$^{-1}$, 718 cm$^{-1}$, 782 cm$^{-1}$ and 856 cm$^{-1}$, which is consistent with the reference [11, 12]. As the addition of Lu$_2$O$_3$, the lattice distortion of Nd: YAG ceramics will be reduced, the symmetry will be further improved, the width of the Raman vibration absorption peak will be significantly narrower, and the intensity of the characteristic peak will be slightly enhanced. (The bands with large changes in Figure 1(c) are marked with arrows). As the doping concentration of Lu$_2$O$_3$ increases, Lu$^{3+}$ with a small radius replaces the position of Y$^{3+}$, which alleviates the lattice distortion caused by Nd$^{3+}$ with a large radius and reduces the structural stress in the crystal. Since all microscopic Raman spectroscopy tests are carried out at room temperature, the broadening of all Raman lines is not related to temperature, but only related to the lattice position and crystal symmetry.

Figure 2(a)-(b) shows the micrographs of the surface and fractured surface of Nd: YAG ceramics sintered at 1750°C for 50 h, respectively. There are no obvious pores on the surface of the sample, the average grain size is about 18 um. Figure 2(c)-(e) shows the EDS spectra of sample S2 and elemental mappings of Nd and Lu, respectively. From the EDS spectra, the element content ratio of Y and Al is close to 5:3, which conforms to the YAG chemical formula. Besides, a minute amount of Nd and Lu elements could be detected in ceramics. The result of the element mapping shows that Nd$^{3+}$ and Lu$^{3+}$ ions were uniformly distributed in the grain boundary and within the grain, and no component segregation appeared.
Figure 2. SEM image of (a) surface, (b) fractured surface, (c) EDS spectra, (d)-(e) Elemental mappings of Nd and Lu from the sample S2.

Figure 3(a) shows the transmittance curve of the ceramic samples. The transmittance curves of the S0-S2 samples are almost the same, and the in-line transmittance is 84.5% at 1064 nm. Based on the size compensation effect, Holloway et al. indicated Lu\(^{3+}\) ion without absorption and emission at the UV-vis wavelength, which was considered as an appropriate size compensation cation compared with the others including Yb\(^{3+}\), Ga\(^{3+}\), Sc\(^{3+}\) [13]. The results indicated that there were no extra absorption peaks from 300 nm to 900 nm in the transmittance curve. The transmittance of S3 and S4 samples slightly decreases in the near-infrared band. Combined with XRD and Raman spectrum analysis, the reason for this phenomenon is excessive Lu\(^{3+}\) doping affects the symmetry of the crystal structure. Compare to the experimental results of Lu et al (Reference 7 and 8), the transmittance of the ceramics samples has been improved largely. Figure 3(b) shows the fluorescence spectrum of the S0-S2 samples. The emission peaks at 1060 nm and 1120 nm belong to the \(^{4}F_{3/2} \rightarrow ^{4}I_{11/2}\) transition of Nd\(^{3+}\) [14]. As the addition of Lu\(_2\)O\(_3\), the shape, and positions of peaks do not change. When the doping concentration of Lu\(_2\)O\(_3\) is 0.02, the fluorescence intensity of the ceramic sample achieved the highest. The fluorescence lifetimes of ceramic samples were measured, as shown in Figure 3(c).

Under the excitation at 808 nm and the emission at 1064 nm, the fluorescence lifetimes of different samples were calculated by the formula (1) [15-17].

\[
I(t) = I_0 \exp \left( -\frac{t}{\tau} \right)
\]  

Where \(I(t)\) is the luminous intensity at time \(t\), \(I_0\) is the emission intensities at time \(t = 0\), \(\tau\) is the fluorescence lifetime, respectively. When \(X = 0.02\), the fluorescence lifetime reaches the maximum value of 193.92 \(\mu\)s. The results indicated that the elimination of lattice distortion is beneficial to the increase of fluorescence lifetime.
Figure 3. (a) Transmission curves, (b) Fluorescence spectra, (c) The decay curves of ceramic samples.

4. Conclusions
In summary, Lu₂O₃ doped Nd: YAG transparent ceramics were successfully fabricated. A small amount of Lu₂O₃ eliminates the lattice distortion by comparing the Raman and XRD spectra of (Nd₀.06LuₓY₂.94₋ₓ)₃Al₅O₁₂ ceramics. When the doping concentration of Lu₂O₃ is 0.02, the fluorescence lifetime of the ceramic sample achieved the highest of 193.92 µs. Besides, Nd³⁺ and Lu³⁺ ions were uniformly distributed in the grain boundary and within the grain. The doping of Lu³⁺ does not affect the spectral characteristics of Nd³⁺. The strain from lattice distortion is relieved because Lu³⁺ ions are doped into the YAG lattice. Lu³⁺ is an effective ion for lattice distortion and has an important effect on the luminescence properties of Nd: YAG ceramics.

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