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Spectroscopy of C_{3i} and C_2 sites of Nd^{3+}-doped Lu_2O_3 sesquioxide either as ceramics or crystal

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ABSTRACT

C_{3i}, C_2 sites and also pairs of Nd^{3+} in Lu_2O_3 ceramics and crystal as laser potential sesquioxides are analyzed.

1. Introduction

Actually one of our research program is dealing with the Lu_2O_3 refractory sesquioxide, which has been suggested to be a potential laser host when doped by Nd^{3+} rare earth ions since a long time, possessing the highest thermal conductivity (12.5 W/m/K) and the lowest phonon energy (391 cm^{-1}) in comparison with YAG (10.8 W/m/K and 700 cm^{-1}, respectively). However, it is extremely difficult to grow Lu_2O_3 single crystal using conventional crystal growth methods because of its high melting point (2490 °C) [1]. It is much easier to fabricate Lu_2O_3 into a ceramic structure since the sintering temperature is about 700 °C lower than its melting point, and no expensive crucible is required [2–5]. As a result, spectroscopic data of Nd^{3+} laser ions are needed in Lu_2O_3 host, either as single crystal or as ceramics. Materials we have analyzed and compared are either Nd^{3+}-doped Lu_2O_3 single crystals grown by the μ-Pulling Down method [1] or Nd^{3+}-doped Lu_2O_3 ceramics fabricated by the non-conventional method Spark Plasma Sintering (SPS) [5] for which we have also shown laser outputs [6]. The main goal of this article is to compare the spectroscopic data of Nd^{3+} ions occupying C_{3i} and C_2 sites of the sesquioxide structure not only in Nd^{3+}-doped Lu_2O_3 ceramics as recently reported [5] but also in Nd^{3+}-doped Lu_2O_3 single crystals.

2. Experimental section

2.1. Materials

2.1.1. Fabrication of the Nd^{3+}-doped Lu_2O_3 ceramics by spark plasma sintering (SPS) method

Powder was put into a graphite die with an inner diameter of 10 mm and then sintered by SPS (SPS-210 LX, SPS Syntex Inc., Kawasaki, Japan) under uniaxial pressures at 20–100 MPa in a vacuum. Pulsed direct current (pulsed of 60 ms on/10 ms off) was applied during sintering. The sintering temperatures varied from 1273 K (1000 °C) to 1823 K (1550 °C) and were held for 300 s to 36 ks at a heating rate of 0.17 K/s.

The Nd^{3+}-doped Lu_2O_3 ceramics were produced from the powder mixtures in a 10-mm-diameter punch, 30-mm-diameter dies and a SPS chamber using multi-step process as follows: (1) the Lu_2O_3 material was heated up to 600 °C under the pressure of 10 MPa within 3 min, (2) it was heated up to 1100 °C with a rate of 100 °C/min, (3) the temperature was hold at 1100 °C for 5 min, (4) the temperature was raised to the sintering temperature of 1450 °C with the heating rate of 10 °C/min under the pressure of

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100 MPa, and (5) the temperature was kept constant for 45 min, and (6) the carbon punch and dies were cooled down. The sintered samples were mirror-polished to thickness of 1 mm. More details can be found in [7,8].

2.1.2. *Growth of the Nd^{3+}-doped Lu_2O_3 crystal by μ-pulling-down technique*

The un-doped and Nd^{3+}-doped Lu_2O_3 single crystals have been grown by the μ-PD method [9–11]. The starting material was Lu_2O_3 powder with 99.99% purity. The growth was performed in the micro-pulling-down apparatus with radiofrequency inductive heating in rhenium crucible with circular die of 5 mm in diameter and five capillary nozzles, which was placed on rhenium after heater and zirconia pedestal. The double-layer zirconia shielding was used for thermal insulation. A mixture of Ar and H_2 gases was used as growth atmosphere. The H_2 concentration was 3%, which is sufficient to prevent rhenium from being oxidized at high temperatures. The gas flow was kept at 1 l/min. The crucible with the starting material was heated up to the Lu_2O_3 melting temperature, which is around 2400 °C. Then, the Lu_2O_3 single-crystal seed was brought into contact with the melt coming through the nozzles due to capillary action. The crystal was pulled at a pulling rate of 0.09 mm/min.

2.2. *Spectroscopic characterization*

2.2.1. *Absorption measurements*

Absorption spectra in the 200–2500 nm spectral range were recorded at 4 K and 293 K with a Cary-Varian 5000 Scan spectrometer equipped with an Oxford CF 1204 helium flow cryostat.

2.2.2. *Emission measurements*

The emission measurements of C_2 and C_{3i} sites at room temperature and 77 K were recorded under selective laser excitation using a CW titanium sapphire laser with the help of an IR Hamamatsu CCD camera and a 900 l/mm grating blazed at 1300 nm.

3. Results

3.1. *Structure of sesquioxides and effect of Nd^{3+} dopant*

The well-known structure of cubic Ln_2O_3 (Ln=Y, Lu, Sc) sesquioxides belongs to the bixbyite type $[^{VI}A_2]$ $[^{IV}O_3]$, which is body-centered cubic, space group $Ia\bar{3}$ with Z= 16. The cubic lattice parameter is 10.391 Å. This type of structure offers two available independent cations sites for the Lu^{3+} atoms with local symmetries C_2 (non-centrosymmetric) and C_{3i} (centrosymmetric), each of them with 6-fold coordination as is shown in Fig. 1. The ratio of C_2 to C_{3i} is 3:1, that is, 32 cations in a unit cell in which 24 occupy C_2 sites and 8 occupy C_{3i} sites. The O^{2-} anions occupy the 48 general positions. The X-ray single crystal structure determination of Lu_2O_3 sesquioxide and of polycrystalline transparent ceramic fabricated by the unconventional spark plasma sintering (SPS) method was reported in [1].

Due to the small difference of ionic radii, trivalent Nd^{3+} (0.983 Å) dopant ions can substitute Lu^{3+} (0.861 Å) ions of the same valency, with slight distortions in the crystal field.

The distribution of the nearest neighbor cations around each C_2 and C_{3i} sites create several possibilities of Nd^{3+} pairs. Table 1 shows the smallest distances between both the C_2 nearest neighbors and the C_{3i} nearest neighbors for Y_2O_3 [12]. Clearly, we assume comparable values for Lu_2O_3. Direct spectra of pairs are experimentally observed only by doping with Yb^{3+} ions characterized by the simplest energy level diagram but not with Nd^{3+} ones having too many energy levels in the UV and visible ranges avoiding any evidence of cooperative luminescence. At around 500 nm we have observed the cooperative luminescence spectra of Yb^{3+} ions in crystals mentioned in Table 2, when the shortest distances between rare earth cations are less than around 4 Å.

The same effect, which should be inferred with Nd^{3+} ions in Lu_2O_3 has been detected by the presence of satellite lines in the foot of the Nd^{3+} 0-phonon absorption lines. Indeed, the creation of Nd^{3+} pairs leads to shifts of absorption lines from isolated Nd^{3+} ions lines mainly due to the different configurations of sites as indicated in Table 2, each individual ensemble producing a distinct crystal field perturbation. These perturbations modify the energy level schemes with respect to those of the unperturbed centers, leading to structures of spectral satellites [12,13]. In the next section the Nd^{3+}-doped Lu_2O_3 ceramics and crystals show quite well-resolved spectral satellites for all the main Nd^{3+} 0-phonon absorption lines with energy shift from the isolated ion lines up to 10 cm^{-1}.

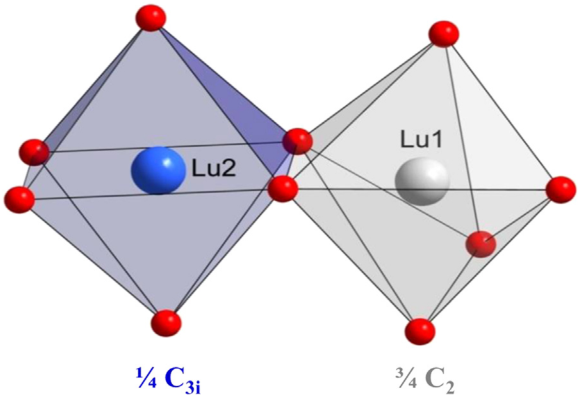

Fig. 1. C_{3i} and C_2 sites of the sesquioxide structure with the occupation ratio of ¼ and ¾ respectively.

Table 1
Distribution of expected Nd^{3+} (or Yb^{3+}) nearest neighbors of C_2 (3/4) and C_{3i} (1/4) site symmetries in Y_2O_3 [12].

	Numbers of sites	Distances in Å
C_2-C_2	4	3.54
	4	4.01
	2	5.30
	4	5.34
C_2-C_{3i}	2	3.52
	2	3.99
C_{3i}-C_2	6	3.52
	6	3.99
C_{3i}-C_{3i}	6	5.3

Table 2
Next neighbor cationic distances of Yb^{3+} pairs in some crystals as detected by cooperative luminescence.

Crystals	Symmetry	Cationic distances of Yb^{3+} pairs	References
Y_2O_3	Cubic (C_2 and C_{3i} symmetry sites)	C_2-C_2=3.54 Å and 4.01 Å	[14]
YAG	Cubic (Y^{3+}:D_2)	3.67 Å	[15]
GGG	Cubic (Gd^{3+}:D_2)	3.78 Å	[16–17]
BaY_2F_8	Monoclinic	3.70 Å	[18]
$LiYF_4$	Tetragonal	3.72 Å	[19]
CaF_2	Cubic	3.84 Å	[20]
KY_3F_{10}	Cubic	3.08 Å	[21]

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