Interband optical transitions in Gd$_2$O$_3$: Er nanoparticles – prospective system for energy convertors

A F Zatsepin$^1$, Yu A Kuznetsova, M A Mashkovtsev and V N Rychkov

Institute of Physics and Technology, Ural Federal University, Yekaterinburg, Russia

$^1$ E-mail: a.f.zatsepin@urfu.ru

Abstract. The features of electron transitions in the region of fundamental absorption edge as well as vibrational characteristics are investigated in Gd$_2$O$_3$ nanoparticles doped with Er$^{3+}$ ions at 0.25-8 mol% concentration. The analysis of initial reflection data is performed for cases of direct and indirect interband transitions. The dependences of corresponding energy gaps on activator concentration are obtained. The effect of strong decrease in the phonon frequency under doping of matrix with a small amount of Er$^{3+}$ is found. The obtained data open new opportunities for improving the efficiency of energy conversion devices.

1. Introduction

Rare earth oxides are of interest as functional materials for energy conversion devices [1]. Gadolinium oxide with a C-type cubic structure attracts special attention as a host matrix due to the chemical and thermal stability and strong paramagnetic behavior [2]. Optically active intrinsic defects of cationic sublattice (irregular Gd$^{3+}$ ions) demonstrate the possibility to donor of UV excitation energy to the activator ions with their subsequent emission in visible spectral region [3, 4]. As an activator ion, Er$^{3+}$ is promising because of intense green and red luminescence and long-lived excited states (millisecond range) [5]. Moreover, for systems containing Er$^{3+}$ ions the anti-Stokes (up-conversion) luminescence can be realized [6, 7]. These features determine prospects of Gd$_2$O$_3$:Er as material for UV and NIR energy convertors.

For optimization and improvement of characteristics of functional devices based on rare earth oxides the information about energy structure of material, electron states, mechanisms of radiative and nonradiative relaxations is needed. It is especially important to consider the features of the interaction between the electron and phonon subsystems because of it determines the key properties of material for optical applications such as absolute quantum and energy yield, kinetics of luminescence quenching, energy conversion efficiency, etc. In this work we investigate the features of interband electron transitions and phonon mode behavior in Gd$_2$O$_3$ nanoparticles under the introduction of Er$^{3+}$ ions.

2. Experimental

Nanopowders of gadolinium oxide doped with Er$^{3+}$ ions in 0.25-8 mol% concentration range were prepared by chemical precipitation method from a water-alcohol solutions of Gd(NO$_3$)$_2$ and Er(NO$_3$)$_3$, followed by annealing at 1000°C during 2 hours. For all investigated samples X-ray diffraction data obtained with the XPert Pro MPD diffractometer correspond to the cubic crystal structure of Gd$_2$O$_3$ without admixtures of any other phases. The unit cell parameter for undoped Gd$_2$O$_3$ is 10.813 Å. Introduction of Er$^{3+}$ ions into the matrix causes to linear decreasing of lattice constant to a value of...
10.793 Å for the Gd$_2$O$_3$:Er (8 mol%) sample with a maximum dopant concentration, which corresponds to the ideal Vegard law for the Gd$_{2-x}$Er$_x$O$_3$ system [8]. The average crystallite size is 55 nm for samples with a low Er$^{3+}$ concentrations (up to 1 mol%) and decreases to 47 nm with a further increase of dopant concentration as was determined by the Debye-Scherrer’s method [9].

Reflectance spectra for all Gd2O3:Er (0.25-8 mol%) samples were obtained using a Perkin Elmer Lambda 35 spectrophotometer equipped with an integrating sphere. For determining spectral dependences of optical density on the basis of primary experimental data we used the Kumar’s analytical model [10]. Analysis of fundamental absorption edge in the regions of direct and indirect interband transitions was performed with use of power-law Tauc’s expression [11].

3. Results and discussion

3.1. Direct and indirect interband transitions

Figure 1 shows the reflection spectra for nanoparticles of nominally pure and activated Gd$_2$O$_3$. A common characteristic of all spectra is the presence of dips in the near-UV region at 276 and 315 nm that correspond to optical absorption in Gd$^{3+}$ ions. Such untypical optical activity for regular cations of matrix indicates the defective nature of Gd$^{3+}$ absorption centers in Gd$_2$O$_3$ as discussed in more detail in our previous works [3, 4]. For activated samples, in reflection spectra there are a number of additional absorption bands in visible and near-IR regions that are identified as 4f-4f intra-configurational transitions in Er$^{3+}$ activator ions. With the increase of concentration, the intensities of corresponding bands increase due to the growth of absorption centers quantity.

![Figure 1. Reflection spectra of nominally pure and Er$^{3+}$-activated Gd$_2$O$_3$ nanoparticles. Absorption bands correspond to electron transitions in Gd$^{3+}$ ($^6\text{S}_{7/2}\rightarrow^6\text{I}_j$, $^6\text{S}_{7/2}\rightarrow^6\text{P}_j$) and Er$^{3+}$ ($^4\text{I}_{15/2}\rightarrow^4\text{I}_{11/2}$, $^4\text{I}_{15/2}\rightarrow^4\text{G}_{11/2}$, $^4\text{I}_{15/2}\rightarrow^4\text{H}_{11/2}$, $^4\text{I}_{15/2}\rightarrow^4\text{F}_{9/2}$, $^4\text{I}_{15/2}\rightarrow^4\text{I}_{9/2}$, $^4\text{I}_{15/2}\rightarrow^4\text{I}_{11/2}$) ions. For clarity, spectra are shifted relative to each other.)](image-url)
The largest dip with a maximum at 220 nm in reflection spectra of all samples is due to the interband optical transitions in Gd₂O₃ matrix. For detailed analysis of behavior of fundamental absorption edge, we use fragments of reflection spectra corresponding to narrow range of wavelengths (225-250 nm) as initial data. Analytical processing of experimental \( R(h\nu) \) reflection data is performed on the basis of Kumar’s model in conjunction with the power-law expression \[ D(h\nu) = \ln[(R_{\text{max}} - R_{\text{min}})/(R(h\nu) - R_{\text{min}})], \] (1)

where \( D(h\nu) \) is the optical density, \( R_{\text{max}} \) and \( R_{\text{min}} \) are the maximum and minimum values of reflection in the selected spectral range, \( n \) is the exponent determining the type of interband transitions (1/2 – for indirect and 2 – for direct transitions).

Since there is no reliable information on the band structure of Gd₂O₃ and it is reported about significantly different values of Gd₂O₃ energy gap (4.85 - 5.9 eV) in the literature [12], we use the equation (1) for the two most probable cases of direct and indirect interband transitions. The obtained results for Gd₂O₃:Er (1 mol%) is presented in the figure 2. Blue circles show the spectral dependence of fundamental absorption edge in the coordinates for direct allowed interband transitions (right scale). Approximation of 5.39-5.45 eV linear range to the intersection with the abscissa axis (as shown by the solid line) gives a value of 5.38 eV, which corresponds to the energy gap for direct band-to-band optical transitions in Gd₂O₃.

**Figure 2.** Optical absorption spectra of Gd₂O₃:Er (1 mol%) nanoparticles in the coordinates for direct (right scale) and indirect (left scale) interband transitions. The arrows show energy gap values for direct and indirect band-to-band transitions with absorption (+ h\( \omega \)) and emission (- h\( \omega \)) of phonons (see inset).

The case of indirect transitions (figure 2, red circles, and left scale) is more complicated. There are two linear regions in 5.15-5.44 eV energy range and, accordingly, two intersection points with the abscissa axis with values of 5.09 and 5.21 eV. It indicates the realization of two types of interband...
transitions – with absorption and emission of phonons, as schematically shown in the inset to figure 2. The midpoint of segment bounded by these points is the $E_g$ (indirect) energy gap, equal to 5.15 eV. Phonon energy ($\hbar \omega$) absorbed and(or) emitted due to the indirect optical transitions in Gd$_2$O$_3$:Er (1 mol%) is 30 meV which corresponds to a frequency of 242 cm$^{-1}$.

Analysis of the fundamental absorption edge for all Gd$_2$O$_3$:Er (0.25-8 mol%) samples allows to reveal a number of regularities. Energy gap for direct interband transitions is invariant to the change of Er$^{3+}$ concentration and equals 5.4 ± 0.02 eV (figure 3(a)). At the same time, small amounts of Er$^{3+}$ ions cause an increase in the energy gap for indirect transitions from 4.93 eV for undoped sample to 5.16 eV for Gd$_2$O$_3$:Er (1 mol%). With further increase of Er$^{3+}$ concentration up to 8 mol%, $E_g$ (indirect) smoothly decreases to 5.08 eV.

![Figure 3. Energy gaps for direct and indirect interband transitions (a) and frequency of phonons involved in indirect optical absorption (b) for Gd$_2$O$_3$:Er (0-8 mol%) nanoparticles as a functions of Er$^{3+}$ concentration.](image)

3.2. Giant phonon softening

The frequency of phonons participating in indirect optical transitions is the most sensitive to the activator’s introduction into the matrix. As can be seen from figure 3(b), introduction of even extremely small amount of Er$^{3+}$ (0.25 mol%) leads to a strong decrease of phonon frequency by more than 1.5 times in comparison with the undoped matrix. The greatest softening of phonon mode is achieved at 1 mol% dopant concentration. Further increase of Er$^{3+}$ amount causes the recovery of phonon frequency to a value of 645 cm$^{-1}$ which is close to the data obtained for pure Gd$_2$O$_3$ matrix (629 cm$^{-1}$).

In the framework of the classical harmonic oscillator model it’s known that frequency of lattice vibrations is directly proportional to the square root of the force constant of atom interaction divided by their reduced mass. Introduction of Er$^{3+}$ ions into the Gd$_2$O$_3$ lattice results in two opposite effects. On the one hand, decrease in the unit cell parameter caused by the replacement of Gd$^{3+}$ cationic positions by Er$^{3+}$ ions with a smaller ionic radius should contribute to increase of vibrational frequency.
On the other hand, increase in the reduced mass resulted from introduction of heavier Er\(^{3+}\) ions into the lattice should cause a decrease in phonon frequency. Quantitative estimation of contributions from these two counteractive effects (\(\Delta \omega_1\) and \(\Delta \omega_2\) ) to the overall theoretical change of phonon frequency (\(\Delta \omega_{th}\)) can be performed using the expression:

\[
\Delta \omega_{th} = \Delta \omega_1 + \Delta \omega_2 = -\omega_0 \left(3 \cdot \gamma \cdot \Delta a/a_0 + \Delta M/2M_o\right),
\]

where \(\omega_0\), \(a_0\) and \(M_o\) - are the phonon frequency, unit cell parameter and reduced mass for undoped \(\text{Gd}_2\text{O}_3\); \(\Delta a\) and \(\Delta M\) - are the absolute changes in lattice constant and reduced mass of \(\text{Gd}_2\text{O}_3\) caused by \(\text{Er}^{3+}\) introduction; \(\gamma\) - is the Grüneisen parameter (1.99 value was used [13]).

The results of calculation (table 1) show that the largest contribution to the phonon frequency change results from the \(\Delta \omega_1\) component that is related to the lattice constant decreasing. The values of \(\Delta \omega_2\) associated with increasing of reduced mass is by two order smaller in comparison with \(\Delta \omega_1\). As a consequence, according to calculations, the vibrational frequency of \(\text{Gd}_2\text{O}_3\) lattice permanently grows with the introduction of \(\text{Er}^{3+}\) ions and the increase in their concentration. The maximum value of phonon frequency shift is 7 cm\(^{-1}\) for sample with 8 mol\% of \(\text{Er}^{3+}\).

Theoretical calculations don’t predict the effect of giant phonon softening that is experimentally observed. Probably, one reason is that calculations take into account behavior of lattice phonon modes only. Whereas experimental phonon softening may be related with the localized defective phonon modes near the structural disorder regions induced by \(\text{Er}^{3+}\) introduction.

**Table 1.** Phonon frequency changes in \(\text{Gd}_2\text{O}_3\) nanoparticles induced by \(\text{Er}^{3+}\) introduction.

\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
\(\text{Er}^{3+}\) concentration, mol\% & 0.25 & 0.5 & 1.0 & 2.0 & 4.0 & 8.0 \\
\hline
\(\Delta \omega_{th}\), cm\(^{-1}\) & 0.475 & 0.537 & 1.078 & 1.944 & 3.536 & 7.137 \\
\hline
\(\Delta \omega_1\), cm\(^{-1}\) & -0.004 & -0.009 & -0.017 & -0.035 & -0.070 & -0.139 \\
\hline
\(\Delta \omega_2\), cm\(^{-1}\) & 0.471 & 0.528 & 1.061 & 1.909 & 3.466 & 6.998 \\
\hline
\(\Delta \omega_{esp}\), cm\(^{-1}\) & -234 & -347 & -387 & -307 & -145 & 16 \\
\hline
\end{tabular}

4. Conclusion

The impact of \(\text{Er}^{3+}\) ions on the electronic-vibrational characteristics of \(\text{Gd}_2\text{O}_3\) matrix was investigated probed by reflection spectroscopy. There are three types of interband optical transitions for both pure and activated \(\text{Gd}_2\text{O}_3\) matrix: (i) – direct transitions; (ii) – indirect transitions with absorption of phonons and (iii) – indirect transitions with emission of phonons. Energy gap for direct transitions doesn’t change with the introduction of \(\text{Er}^{3+}\) ions, while the energy gap for indirect absorption increases and achieves a maximum at 1 mol\% of \(\text{Er}^{3+}\) concentration.

The phonon frequency is the most sensitive to the introduction of the activator into the lattice. The effect of giant phonon softening in \(\text{Gd}_2\text{O}_3\) with a small amount of \(\text{Er}^{3+}\) ions was experimentally observed, however, theoretical calculations don’t predict it. According to the preliminary forecast, this phenomenon can be associated with the local defective phonon modes induced by the \(\text{Er}^{3+}\) introduction into the \(\text{Gd}_2\text{O}_3\) lattice. The obtained data indicate the possibility of thermal losses minimization during the radiation conversion. This allows improving the functional characteristics of energy convertors and increasing their efficiency.
Acknowledgments
The work has been funded by the Ministry of Education and Science (Government task №3.1485.2017/4.6) and by Act 211 Government of the Russian Federation, contract 02.A03.21.0006.

References
[1] Liu G K and Chen X Y 2007 Handbook on the Physics and Chemistry of Rare Earths vol 37, ed. K A Gschneidner Jr, J C G Bunzli and V K Pecharsky (North-Holland: Amsterdam, The Netherlands) 99
[2] Li H, Song S and Wang W 2015 Dalton Trans. 44(36) 16081–16090
[3] Kuznetsova Yu A, Zatsepin A F, Tselybeev R A et all 2016 J. Phys. Conf. Ser. 741(1)
[4] Zatsepin A, Kuznetsova Yu, Spallino L et al 2016 Energy Proc. 102 144-151
[5] Chen X, Ma E, Liu G and Yin M 2007 J. Phys. Chem. C 111(27) 9638–9643
[6] Mangiarini F, Nacache R, Speghini A et al 2010 Mater. Res. Bull. 45 927-932
[7] Trofimova E S, Pustovarov V A, Kuznetsova Yu A and Zatsepin A F 2017 AIP Conf. Proc. 1886 020024
[8] Vegard L 1921 Zeitschrift fü r Physik 5(1) 17-26
[9] Klug P and Alexander L E 1954 X-ray Diffraction Procedure (New York: Wiley)
[10] Kumar V, Sharma T P and Singh V 1999 Opt. Mater 12 115–119
[11] Tauc J 1974 Amorphous and Liquid Semiconductors (Plenum, New York)
[12] Gillen R, Clark S J and Robertson J 2013 Phys. Rev. B 87 125116
[13] Sharma D N, Singh J, Vijay A et al 2016 J. Phys. Chem. C 120(21) 11679-11689