IOP Conf. Series: Journal of Physics: Conf. Series **917** (2017) 062001 doi:10.1088/1742-6596/917/6/062001

Optical properties and energy parameters of Gd_2O_3 and Gd_2O_3:Er nanoparticles

Yu A Kuznetsova, A F Zatsepin,
Institute of Physics and Technology, Ural Federal University, Yekaterinburg, Russia

Abstract. The reflection spectra of Gd_2O_3 and Gd_2O_3:Er nanoparticles have been investigated. Several types of absorption centers associated with Er^{3+} activator ions and intrinsic lattice defects have been revealed. It was found that interband absorption is formed by indirect optical transitions with participation of phonons. The values of energy gap and phonons energy were determined.

1. Introduction

Low-dimensional modifications of gadolinium oxide are of interest as functional materials for devices of nanophotonics, optoelectronics, alternative energy and systems of radiation conversion [1,2]. The important fundamental parameter that determines optical properties of material is the band gap. The most common way for obtaining this parameter is to use the data of absorption spectrum. However, in some cases a direct measurement of optical absorption is difficult due to the features of samples structure (nontransparent powders, compacts, ceramics). The main purpose of the present work is to realize an alternative method for determining the band gap value of Gd_2O_3 compacted nanopowders on the basis of reflection spectra analysis.

It is known that development of rare-earth based materials for devices of radiation conversion requires the introduction of single or paired activator ions into the host lattice, for example Eu^{3+}, Tb^{3+}, Yb^{3+}/Er^{3+}, Yb^{3+}/Ho^{3+} [3,4]. In this regard, it is necessary to understand the impact of dopants on the optical characteristics of matrix. The second task of this work is devoted to establishing the influence of Er^{3+} activator ions on formation of energy structure of Gd_2O_3 host lattice.

2. Experimental

The Gd_2O_3 and Gd_2O_3:Er (2 mol%) compacted nanopowders were obtained from aqueous solutions of $Gd(NO_3)_2$ and $Er(NO_3)_2$ precursors by chemical precipitation method followed by pressing and annealing at 1000°C. The diffraction peaks in XRD patterns of both samples correspond to the cubic single-phase structure of Gd_2O_3 (Ia-3 space group). The average crystalline grains sizes were estimated to be of 30-40 nm. Reflection spectra were recorded on a Lambda 35 spectrophotometer equipped by integrating sphere.

3. Results and discussion

3.1 Reflection spectra

Reflection spectrum of Gd_2O_3 (figure 1, blue) contains a number of absorption bands in the near UV region. The most intense band with a maximum at 220 nm corresponds to interband transitions of Gd_2O_3 matrix [5]. The lines at 276 and 315 nm can be attributed to the 4f-4f optical transitions of Gd^{3+}

ion from the ground $^8S_{7/2}$ to the excited ^6I_J and ^6P_J states correspondingly. Selective absorption peaks of the host lattice cations indicate that energy structure of a part of Gd^{3+} ions in Gd_2O_3 is distorted, in other words, such ions represent intrinsic defective optical centers [6].

As reflection spectrum for Gd_2O_3:Er shows (figure 1, red), introduction of Er^{3+} ions into the gadolinium oxide host lattice results in the appearance of additional absorption peaks in visible and near-infrared spectral regions. Along with the bands of interband transitions and absorption in Gd^{3+} ions the lines at 380, 523, 655, 802 and 977 nm are clearly observed. These bands correspond to the optical transitions in Er^{3+} ions from the ground $^4I_{15/2}$ to the excited $^4G_{11/2}$, $^2H_{11/2}$,$^4F_{9/2}$, $^4I_{9/2}$ and $^4I_{11/2}$ energy levels [7]. Based on the primary experimental data obtained from the reflection spectra, one can conclude that there are at least two types of absorption centers in Gd_2O_3:Er nanoparticles: intrinsic defective Gd^{3+} ions and Er^{3+} activator ions.

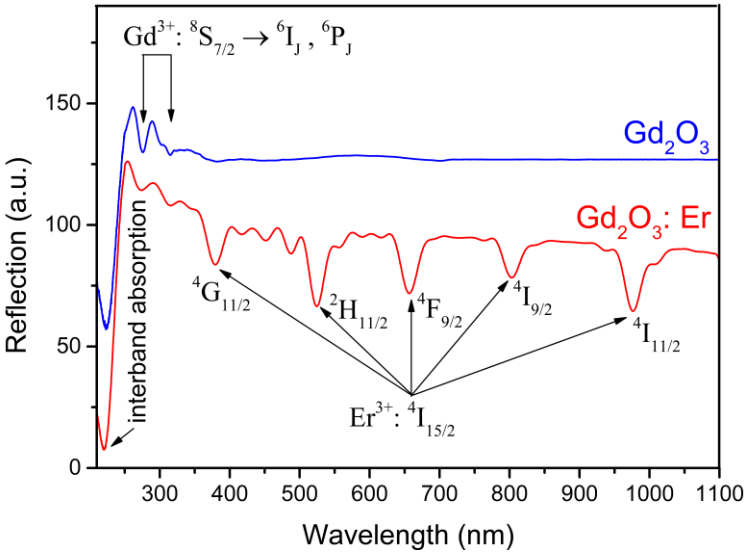

Figure 1. Reflection spectra of Gd_2O_3 (blue) and Gd_2O_3:Er (red) nanoparticles. The optical transitions corresponding to absorption in Gd^{3+} and Er^{3+} ions are shown by arrows.

3.2 Absorption spectra and parameters of energy structure

Spectral dependences of absorption coefficient $\alpha(h\nu)$ can be obtained by the analysis of reflectance experimental data $R(h\nu)$ in accordance with the models proposed by Kumar [8] and Kubelka-Munk [9] by using following analytical equations:

$$\alpha(h\nu) = \ln[(R_{\max} - R_{\min})/(R(h\nu) - R_{\min})]/2d \quad (1)$$

$$F(h\nu) = (1 - R(h\nu))^2 / 2R(h\nu) \quad (2)$$

where $R_{\max}$ and $R_{\min}$ are maximum and minimum values of reflectance, d is the thickness of the absorption layer, $F(h\nu)$ is the Kubelka-Munk function that is directly proportional to the absorption coefficient. At the same time, the dependence of the absorption coefficient on the energy of the incident photons can be described by the power-law expression [10]:

$$\alpha(h\nu) \cdot h\nu = A(h\nu - E_g)^n \quad (3)$$

where A is a constant, E_g is the energy gap, n is the exponent that determines the type of interband transitions (1/2; 3/2; 2 and 3 for direct and indirect allowed and forbidden transitions respectively).

Since the information about the energy structure and nature of the interband transitions in Gd_2O_3 is limited, we performed the approximation of absorption data obtained in accordance with both Kumar's and Kubelka-Munk's models by equation (3) setting the parameter n as a variable. The best fitting (the correlation coefficient was 0.996) has been achieved with the n values of 2.3 and 2.4 for Gd_2O_3 and

Gd_2O_3:Er samples correspondingly. It indicates the realization of indirect interband transitions as for the undoped Gd_2O_3 matrix as for the sample activated by the Er^{3+} ions.

In order to obtain the energy gap values we carried out the analysis of spectral dependences of absorption determined by using the Kubelka-Munk's and Kumar's approaches in the coordinates of indirect optical transitions (figure 2 and figure 3).

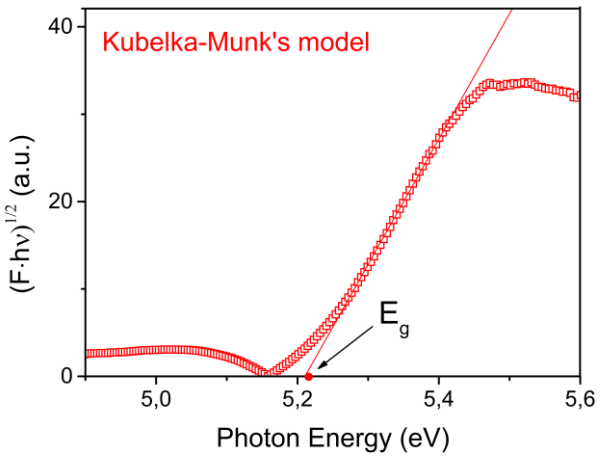

Figure 2. Absorption spectra of Gd_2O_3:Er nanoparticles for indirect transitions in accordance with the Kubelka-Munk's model [9]. Arrow indicates the value of energy gap E_g.

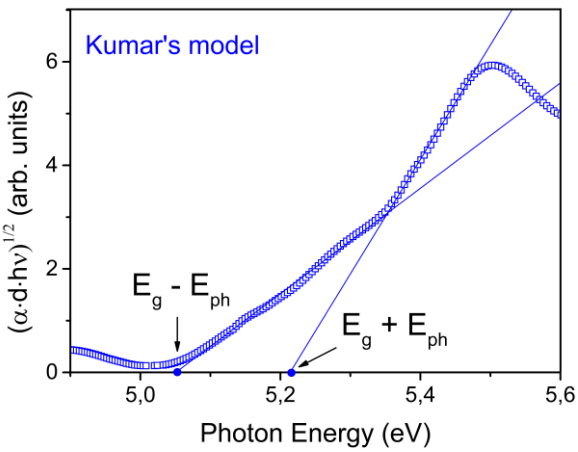

Figure 3. Absorption spectra of Gd_2O_3:Er nanoparticles for indirect transitions in accordance with the Kumar's model [8].The energy gap values (E_g) for transitions with absorption and emission of phonons (E_{ph}) are marked by arrows.

The approximation of linear range in the spectral dependence of Kubelka-Munk's function by straight line up to the crossing with the abscissa axis allows determining the energy gap for indirect transitions that is found to be of 5.09 and 5.21 eV for Gd_2O_3 and Gd_2O_3:Er nanoparticles respectively. In the case of using the Kumar's model a more complex features are observed (figure 3). The absorption spectrum is characterized by the two linear regions. Coordinates of crossing points with the energy axis correspond to the values E_g+E_{ph} and E_g-E_{ph} where E_g is the energy gap between maximum of valence band and minimum of conduction band, E_{ph} is the energy of phonons that participate in the indirect optical transition [11]. In other words, there are two types of indirect transitions: with absorption and with the emission of phonons. In figure 4 the schematic representation of these transitions is presented. The obtained values of energy gap and phonon energy for Gd_2O_3 and Gd_2O_3:Er nanoparticles are summarized in table 1.

Table 1. The values of energy gap and phonons energy obtained under fitting the reflectance experimental data in accordance with the Kumar's and Kubelka-Munk's models for Gd_2O_3 and Gd_2O_3:Er nanoparticles.

Sample	*Kumar's model (Equation (1))*		*Kubelka-Munk's model (Equation(2))*
	E_g , *eV*	E_{ph} , *meV*	E_g , *eV*
Gd_2O_3	4.97	78	5.09
Gd_2O_3:Er	5.13	80	5.21

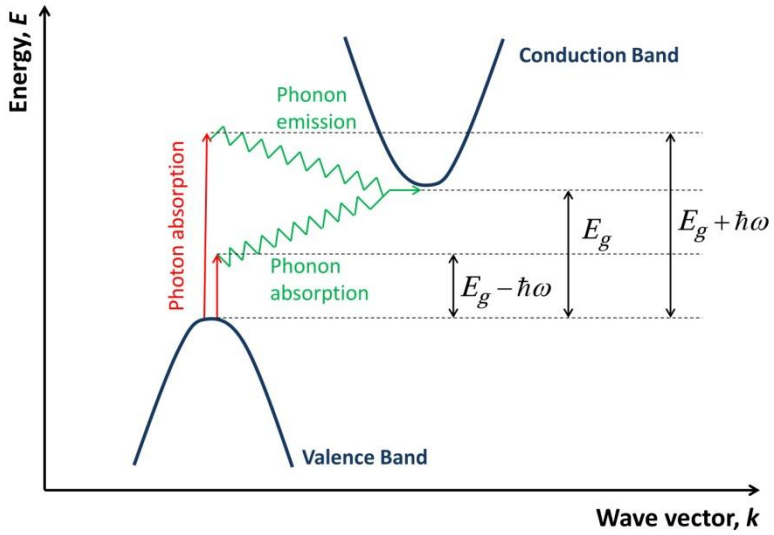

Figure 4. Schematic representation of indirect interband transitions with absorption and emission of phonons in Gd_2O_3 and Gd_2O_3:Er nanoparticles.

4. Conclusion

In present work we have demonstrated an approach to the determination of the spectral characteristics of absorption centers, the type of interband transitions, and the energy gap value for low-dimensional modification of gadolinium oxide based on the data of reflection spectra. Several types of optically active absorption centers have been revealed in Gd_2O_3 and Gd_2O_3:Er nanoparticles: intrinsic defective Gd^{3+} ions and Er^{3+} activator ions. It was found that the absorption edge of Gd_2O_3 at room temperature is formed by the phonon-assisted indirect optical transitions. The effect of increasing of Gd_2O_3 band gap under the activation by Er^{3+} ions has been detected.

Acknowledgments

The work has been funded by the Ministry of Education and Science of the Russian Federation (Government task №3.1485.2017/PP).

References

[1] Tamrakar R K, Bisen D P, Brahme N 2014 *Res. Chem. Intermediat*. **40** 1771-1779
[2] Anishur Rahman A T M, Vasilev K, Majewski P 2011 *J. Colloid. Interf. Sci*. **354** 592-596
[3] You L, Wang S, Ren B et all 2016 *J. Nanosci. Nanotechno*. **16** 9731-9737
[4] Li D, Qin W, Aidilibike T et all 2016 *J. Alloy. Compd*. **675** 31-36
[5] Ferrara M C, Altamura D, Schioppa M et all 2008 *J. Phys. D Appl. Phys.* **41** 225408
[6] Zatsepin A F, Kuznetsova Yu A, Spallino L et all 2016 *Energy Proc*. **102** 144-151
[7] Jia D, Lu L, Yen W M 2002 *Opt. Commun*. **212** 97-100
[8] Kumar V, Sharma T P, Singh V 1999 *Opt. Mater* **12** 115–119
[9] Kubelka P, Munk F 1931 *J. Tech. Phys*. **12** 593
[10] Tauc J 1974 *Amorphous and Liquid Semiconductors* (Plenum, New York)
[11] Wakaki M, Shibuya T, Kudo K 2007 *Physical Properties and Data of Optical Materials* (CRC Press Taylor & Francis Group)