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Energy transfer and upconversion luminescence properties of Y_2O_3:Sm and Gd_2O_3:Sm phosphors

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Abstract

Y_2O_3:Sm and Gd_2O_3:Sm powder phosphors were prepared by carbonate coprecipitation method. The purified crystalline phases of Y_2O_3:Sm and Gd_2O_3:Sm were obtained at 600°C, and the crystallinity increases with increase in annealing temperature. Both samples contain aggregated phosphor particles. An energy transfer (ET) from Y_2O_3 and Gd_2O_3 hosts to sm^{3+} has been observed, and the ET efficiency in the latter is higher than that in the former because an energy migration process like Gd^{3+}–$(Gd^{3+})_n$–Sm^{3+} has occurred in the latter. Furthermore, an upconversion luminescence from the $^4G_{5/2}$ level of Sm^{3+} has been observed in both Y_2O_3 and Gd_2O_3 under the excitation of 936 nm infrared, whose mechanisms are proposed. Both the up and downconversion emission intensities of Sm^{3+} in Gd_2O_3 are stronger than those in Y_2O_3.

Keywords: Yttrium oxide; Gadolinium oxide; Samarium; Luminescence; Energy transfer; Upconversion

1. Introduction

An upconverting phosphor is one, which takes multiple photons of lower energy and converts them to one photon of higher energy [1,2]. Recently, as the upconversion phenomena in rare-earth-doped systems are useful for developing efficient short-wavelength solid-state lasers, there has been renewed interest in rare-earth-ions doped solid-state materials which can transform infrared radiation into visible emission [3,4]. However, very little is known about the upconversion properties of Sm^{3+} [5–8]. As commercial phosphors, Eu^{3+}-doped Y_2O_3 and Gd_2O_3 have been extensively studied. But very little study has been done on the luminescence and energy transfer (ET) properties for Sm^{3+} in these rare-earth oxides. The only related report is the crystal field study on Gd_2O_3:Sm^{3+} and Y_2O_3:Sm^{3+} by Martel et al. [9]. In this paper, we report the ET and upconversion luminescence properties of Gd_2O_3:Sm^{3+} and Y_2O_3:Sm^{3+} phosphors prepared by carbonate coprecipitation method.

2. Experimental

All the rare-earth oxides Y_2O_3 (99.99%), Gd_2O_3 (99.99%) and Sm_2O_3 (99.9%) were purchased from Shanghai Yuelong Non-Ferrous Metal Limited Company. Sodium carbonate (Na_2CO_3, A.R.) was used as precipitant. Certain amounts of Y_2O_3, Gd_2O_3 and Sm_2O_3 were dissolved in diluted HNO_3 (A.R) to obtain stock solutions. Typically, 50 mL 0.2 M Na_2CO_3 aqueous solution was dropped slowly into 50 mL 0.2 M mixed solution of $Y(NO_3)_3$ and/or $Gd(NO_3)_3$ and $Sm(NO_3)_3$ in a beaker under magnetic stirring. The doping concentration of Sm^{3+} is 3 mol% that of Y^{3+} (or Gd^{3+}). The resultant suspension was homogenized for 0.5 h and precipitation occurred. The obtained precipitate was centrifuged and washed with distilled water three times, then dried at 60°C for 24 h. The dried precursor was then grounded in an agate mortar and calcined under certain temperatures (500–900°C) in air.

Phase development in the post-annealed powder samples were checked by X-ray diffraction (Rigaku, D/max-II B) using Cu$K\alpha$ radiation ($\lambda = 0.15405$ nm). The morphology of the crystalline samples was inspected using a scanning electron microscope (JEOL JXA-840). The excitation and emission spectra were

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taken on a Hitachi F-4500 spectrofluorimeter equipped with a 150 W xenon lamp as the excitation source. The upconversion luminescence spectra were measured on a SPEX FL-2T2 spectrofluorimeter equipped with a 450 W xenon lamp as the excitation source. Luminescence lifetimes were measured with a SPEX 1934D phosphorimeter using a 7 W xenon lamp as the excitation source with the pulse width of 3 μs. All the measurements were performed at room temperature (RT).

3. Results and discussion

3.1. Structures and morphology of Gd_2O_3:Sm^{3+} and Y_2O_3:Sm^{3+}

Pure cubic phase of Gd_2O_3:Sm^{3+} and Y_2O_3:Sm^{3+} are obtained when the annealing temperature is 600°C, and the crystallinity increases with the increase of annealing temperature. Fig. 1 shows the representative X-ray diffraction patterns of Gd_2O_3:Sm^{3+} and Y_2O_3:Sm^{3+} annealed at 900°C. All the peaks are corresponding to the cubic Gd_2O_3 (JCPDS card 12-797) and Y_2O_3 (JCPDS card 25-1200). No second phase can be detected, indicating that the doped Sm^{3+} ions have entered the Gd^{3+} and Y^{3+} sites completely. The crystalline grain size of Gd_2O_3:Sm^{3+} and Y_2O_3:Sm^{3+} have been calculated using the Scherrer equation, $d = 0.941\lambda/B\cos\lambda_B$, where λ is the X-ray wavelength (0.15405 nm), B is the FWHM of the Bragg peak, λ_B is the Bragg angle. The strongest (222) peak was used to calculate the d values at different annealing temperatures. It is shown that crystalline grain size (25–55 nm) of Gd_2O_3:Sm is larger than that (25–35 nm) of Y_2O_3:Sm, both of which increase with increasing the annealing temperatures, as shown in the inset of Fig. 1.

Fig. 2 shows the SEM micrographs of the Gd_2O_3:Sm (a) and Y_2O_3:Sm (b) samples annealed at 900°C. It can be seen that both samples contain aggregated particles. Due to the aggregation, the grain size observed in SEM is much larger than that calculated from the Scherrer equation.

3.2. Energy transfer properties in Y_2O_3:Sm and Gd_2O_3:sm

Under short-wavelength ultraviolet excitation, both Y_2O_3:Sm and Gd_2O_3:Sm phosphors show a red emission, and the emission intensity of the former is weaker than that of the later. This phenomenon can be well understood by measuring the excitation spectra of

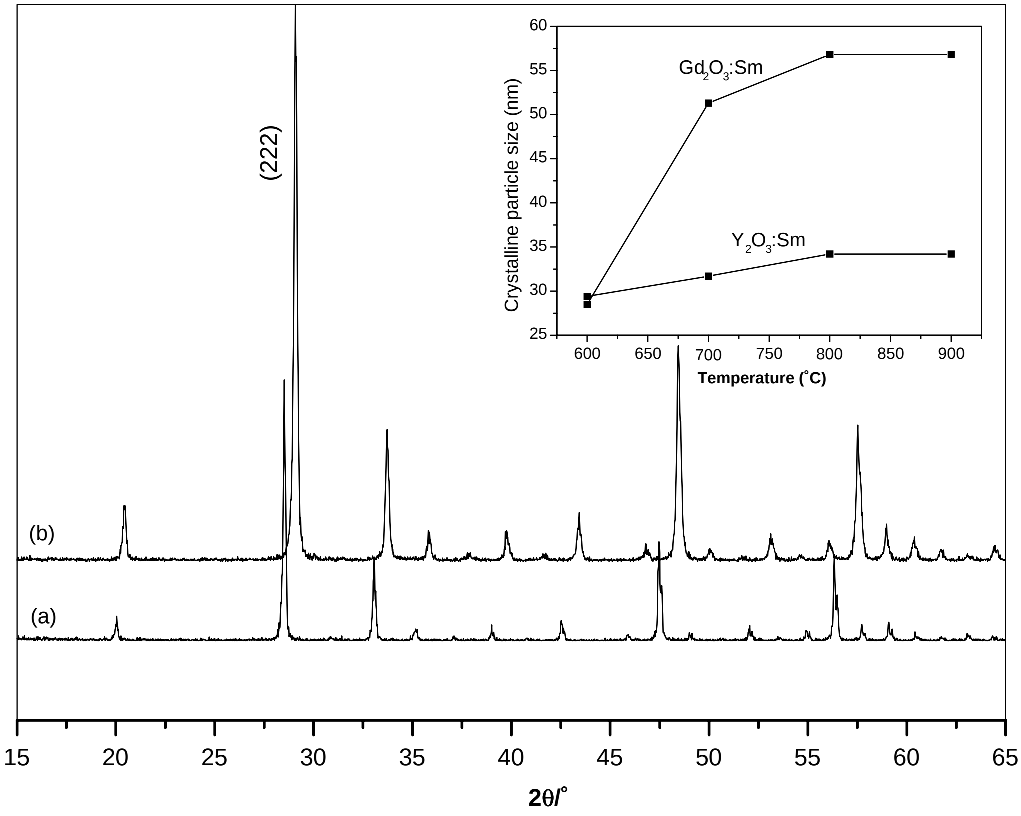

Fig. 1. XRD patterns of Gd_2O_3:Sm (a) and Y_2O_3:Sm (b) annealed at 900°C. The inset shows the change of crystalline grain size as a function of the annealing temperatures.

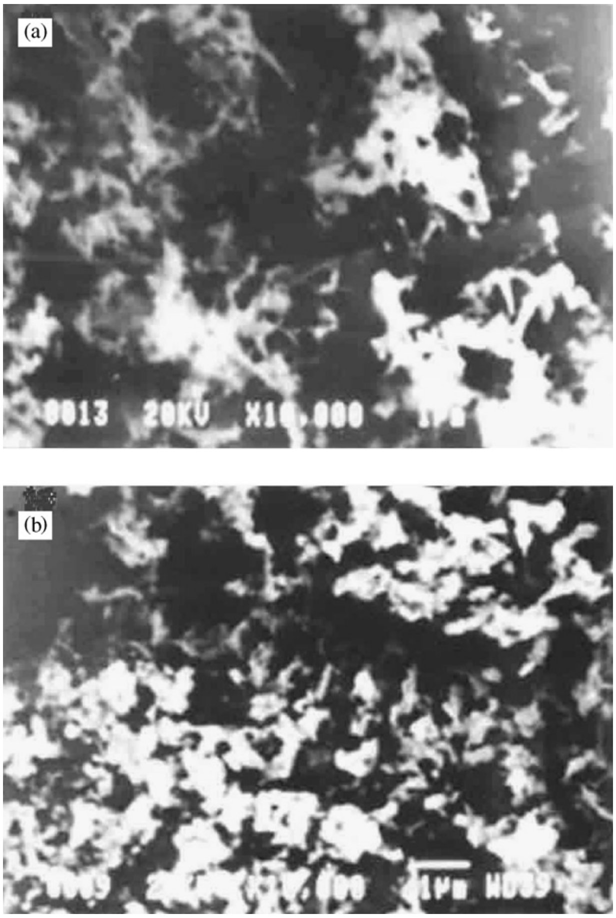

Fig. 2. SEM micrographs of Gd_2O_3:Sm (a) and Y_2O_3:Sm (b) annealed at 900°C.

$Y_{1.97(1-x)}Gd_{1.97x}O_3:Sm_{0.03}$ $(0 \leqslant x \leqslant 1)$, as shown in Fig. 3a. The excitation spectra consist of three parts, i.e., a broad band from 200 to 250 nm with the strongest intensity, a group of excitation lines peaking at 257 nm (^8S–^6D), 278 nm (^8S–^6I) and 316 nm (^8S–^6P) for Gd^{3+}, and a group of weak $f-f$ transition lines within the Sm^{3+} $4f^5$ configuration with the most intense one peaking at 409 nm ($^6H_{5/2}$–$^4K_{11/2}$). Here it is interesting to note that the maximum values of the broad excitation bands in the short UV region shift to longer wavelengths and increase in intensity with the increase of x values, i.e., from 215 nm for $x = 0(Y_2O_3:Sm)$ to 234 nm for $x = 1(Gd_2O_3:Sm)$. There are two possibilities for the assignments of the UV excitation bands, i.e., charge transfer band for Sm^{3+}–O^{2-} bond or absorption of the oxide host lattices. In order to assign the broad UV excitation bands, we deposited a transparent pure Gd_2O_3 thin film on silica glass by sol–gel process and measured the UV/vis absorption spectrum, as shown in the inset of Fig. 3a. The pure Gd_2O_3 film also presents a strong absorption from 200 to 250 nm, so we believe that the broad band in the excitation spectra is from the oxide host lattices. The charge transfer band of Sm^{3+}–O^{2-} should be below 200 nm considering the difficulty in the electron transfer from O^{2-} to Sm^{3+} with the $4f^5$ electronic configuration. Blasse [10] also pointed out that the broad excitation band between 200 and 230 nm in $Y_2O_3:Eu^{3+}$ is due to the absorption of Y_2O_3 host lattices. Because the ionic radius (0.0938 nm for six-coordination) of Gd^{3+} is larger than that (0.090 nm for six-coordination) of Y^{3+}, the bond length of Gd–O is longer than that of Y–O, resulting in the absorption energy Gd_2O_3 being lower than that of Y_2O_3.

The presence of the strong excitation bands of the Y_2O_3 and Gd_2O_3 host lattices indicates that there exists an efficient ET from the Y_2O_3 and Gd_2O_3 host lattices to the Sm^{3+} ion, and the ET from the Gd_2O_3 host to Sm^{3+} seems more efficient than that from the Y_2O_3 host to Sm^{3+} according to Fig. 3a. In Fig. 3a, the intensity of Gd^{3+} excitation lines (^8S–^6D, ^6I, ^6P) increase monotonically with increase of x values, suggesting that an energy migration process like Gd^{3+}–$(Gd^{3+})_n$–Sm^{3+} occurs, as observed previously by Lin and Su [11] and others [12,13]. The emission spectra of $Gd_{1.97}O_3:Sm_{0.03}$, $Y_{0.985}Gd_{0.985}O_3:Sm_{0.03}$ and $Y_{1.97}O_3:Sm_{0.03}$ under excitation of 234 nm UV light are shown in Fig. 3b. It can be seen that the emission intensity of Sm^{3+} increases greatly from $Y_{1.97}O_3:Sm_{0.03}$ via $Y_{0.985}Gd_{0.985}O_3:Sm_{0.03}$ to $Gd_{1.97}O_3:Sm_{0.03}$. In this case, the excitation energy is absorbed by the oxide host, then transferred to Gd^{3+} and via Gd^{3+}–$(Gd^{3+})_n$ process, trapped by Sm^{3+} finally. These ET and energy migration processes are blocked by diluting the Gd^{3+}-sublattice with Y^{3+}, resulting in the decrease of the emission intensity of Sm^{3+} in the oxides containing Y^{3+}. The lifetimes of Sm^{3+} $^4G_{5/2}$ excited state are 0.58 and 0.88 ms in $Y_{1.97}O_3:Sm_{0.03}$ and $Gd_{1.97}O_3:Sm_{0.03}$, respectively.

3.3. Upconversion properties of Y_2O_3:Sm and Gd_2O_3:Sm

The upconverted luminescence phenomena of Sm^{3+} have been observed in Y_2O_3:Sm and Gd_2O_3:Sm. Fig. 4 shows the upconverted emission and excitation spectra of Sm^{3+} in Y_2O_3:Sm and Gd_2O_3:Sm. Infrared 936 nm excitation yields emission spectra of Sm^{3+} from 500 to 700 nm, corresponding to the electronic transitions of Sm^{3+} $^4G_{5/2}$–$^6H_{5/2}$ (572 nm), $^4G_{5/2}$–$^6H_{7/2}$ (609 nm) and $^4G_{5/2}$–$^6H_{9/2}$ (656 nm), respectively. The infrared excitation spectra of Sm^{3+} are shown in Fig. 4b, which contain two main peaks at 936 and 954 nm corresponding to Sm^{3+} $^6H_{5/2}$–$^6F_{11/2}$ and $^6H_{5/2}$–$^6F_{9/2}$, respectively. The Sm^{3+} also shows a stronger upconversion emission intensity in Gd_2O_3 than in Y_2O_3.

To our knowledge, the upconversion for Sm^{3+} has only been reported in low-phonon-energy hosts such as GdOCl [5–8]. It is the first observation for the upconversion phenomenon of Sm^{3+} in Gd_2O_3 and Y_2O_3 hosts. Under infrared 936 nm excitation, the $^4G_{5/2}$ excited state of Sm^{3+} can be populated by two possible approaches: the excited state absorption (EAS) and ET

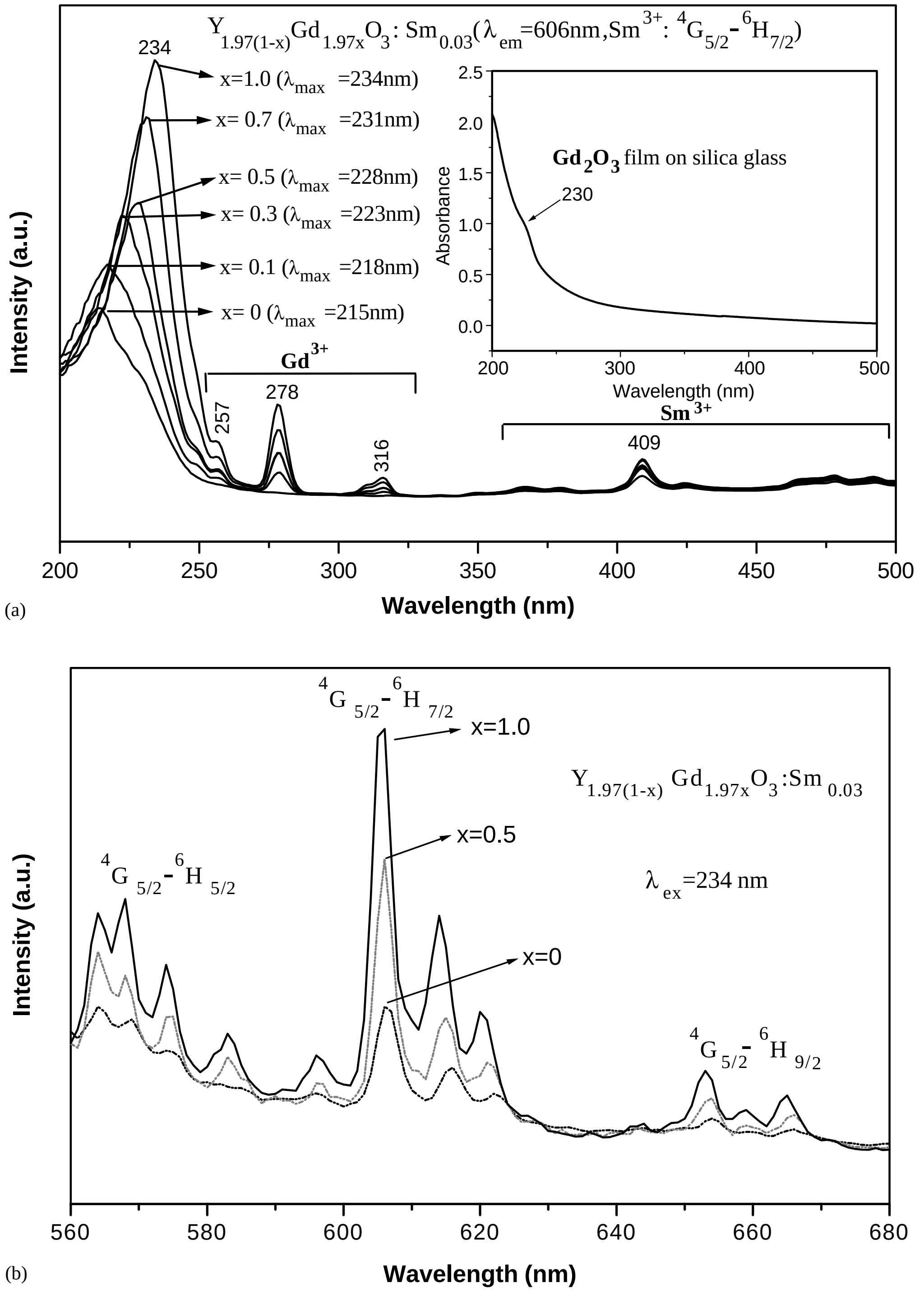

Fig. 3. Excitation (a) and emission spectra of $Y_{1.97(1-x)}Gd_{1.97x}O_3$:$Sm_{0.03}$. The inset in Fig. 3a shows the UV/v is absorption spectrum of Gd_2O_3 film on silica glass.

processes, as shown in Fig. 5. For the ESA process (a), after a first excitation to the $^6F_{11/2}$ level, a second photon is absorbed by the same ion, exciting it to $^4I_{11/2}$ state, i.e., $^6H_{5/2} \rightarrow {}^6F_{11/2} \rightarrow {}^4I_{11/2}$; for the ET process [(b)+(c)], one of the two coupled Sm^{3+}, simultaneously excited through the ground state absorption by infrared photons to the $^6F_{11/2}$ state, transfers its energy to the neighboring ion leaving it in the higher excited states ($^4I_{11/2}$, etc). Both approaches excite the Sm^{3+} to $^4I_{11/2}$ (or $^4G_{7/2}$, $^4F_{3/2}$) state, from which $^4G_{5/2}$ energy level is populated by multiphonon de-excitation. As a result, anti-stokes emissions from $^4G_{5/2}$ excited state to the ground states ($^6H_{5/2}$, $^6H_{7/2}$, $^6H_{9/2}$) are observed. In view of the short lifetime (the order of 10 ns) of $^6F_{11/2}$ level of Sm^{3+}, ESA transitions from this level are not likely to occur [14]. So the most probable mechanism for the

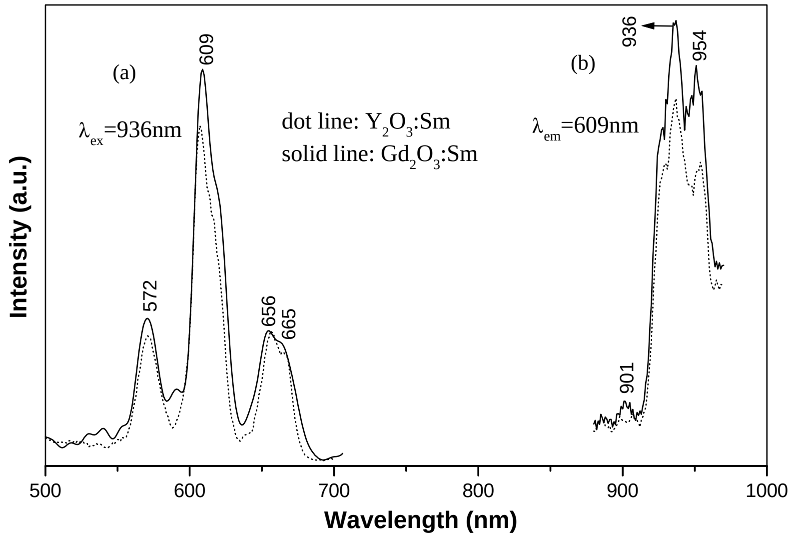

Fig. 4. Upconversion emission (a) and excitation (b) spectra of Y_2O_3:Sm and Gd_2O_3:Sm.

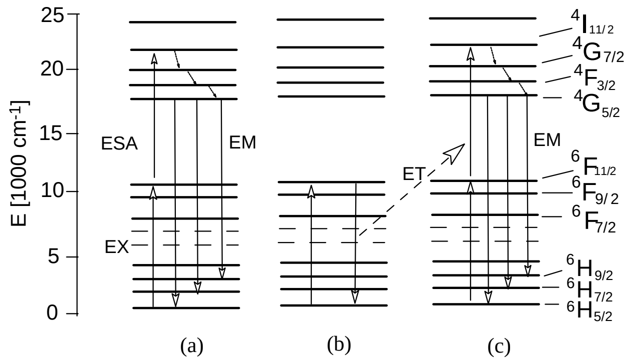

Fig. 5. Schematic diagram of ESA and ET approaches for the upconversion of Sm^{3+}.

upconversion luminescence of Sm^{3+} in Y_2O_3 and Gd_2O_3 hosts is ET between two Sm^{3+} ions.

4. Conclusions

RE$_2$O$_3$:Sm^{3+} (*RE*=Y, Gd) powder phosphors were prepared successfully by carbonate coprecipitaion method. There exists an ET from the oxide hosts to the doped Sm^{3+}, and the ET efficiency is more efficient in the Gd_2O_3 than in Y_2O_3 because an energy migration process like Gd^{3+}–$(Gd^{3+})_n$-Sm^{3+} occurs in the former. As a result, the Sm^{3+} presents higher emission intensity in Gd_2O_3 than in Y_2O_3. The upconversion emission from Sm^{3+} $^4G_{5/2}$ has been observed for the first time under the excitation of an infrared 936 nm in Gd_2O_3 and in Y_2O_3, and the upconversion emission is mainly attributed to ET between two Sm^{3+} ions.

Acknowledgments

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