

Near infrared and visible luminescence in transparent (Er, Yb)- α -sialon ceramics under 980 nm laser irradiation

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The novel Er^{3+} and Yb^{3+} doped transparent Sialon ceramics were fabricated by hot pressing sintering method as a near infrared (NIR) as well as visible luminescent material. The optical transmittance, down-conversion luminescence and NIR luminescence were investigated. The samples show around 30% transmittance in visible region whereas 70% in IR region around 3000 nm. The samples were excited within the range of 350–400 nm wavelength, the highest emission was in green region (~550 nm). Also, the upconversion luminescence depending upon the thicknesses of the samples in the green and red region have been investigated. The NIR luminescence was observed around 1524 nm wavelength under 980 nm wavelength irradiation. The decay time profiles have been investigated for higher Er^{3+} concentration and higher Yb^{3+} co-doped with Er^{3+} α -Sialon samples. In this study, the addition of Yb^{3+} has poor sensitizing effect on Er^{3+} ion to enhance the luminescence.

Key words: α -Sialon, NIR luminescence, Hot press, Transmittance.

Introduction

There are few transparent polycrystalline ceramics that have been studied as a luminescent material [1–3]. And even few IR luminescent ceramics are studied [1, 4]. In the field of communication as well as IR laser, these transparent ceramics can be useful if they show particular luminescence in IR spectrum. The Er^{3+} doped transparent materials are essential for obtaining luminescence around 1500 nm lasers. These IR lasers are utilized for long distance telemetry and ranging based on considerations of atmospheric transparency and eye safety.

The single crystals, transparent polycrystalline oxide ceramics, glasses and some polymers are studied for telemetry and laser purposes [1, 4–6]. The poor chemical stability and low laser induced damage threshold of glasses and polymers make less efficient and applications are limited. In other hand, the single crystals and transparent polycrystalline ceramics have excellent chemical stability and high laser induced damage threshold. Moreover, the polycrystalline transparent ceramics surpasses the single crystals due to their low cost, multifunctional structures and ease of fabrication.

The mostly studied polycrystalline ceramics as a lasening materials are garnet system i.e. YAG and LuAG doped with different rare earth ions [1, 7]. These garnets have cubic crystal structure and phonon energy of cubic crystal system is high and not efficient to those of hexagonal system [8]. Therefore, there is

always search for the new host transparent ceramics for better performance.

In the present work, we fabricated a novel IR luminescent polycrystalline transparent Sialon ceramics. The Sialon ceramics are hexagonal in crystal structure and have low phonon energy [9]. There were some researches carried out in the Sialon ceramics as a transparent material [10–13]. However, no such improvement in transmittance was observed in previous studies. The thin sample shows good transmittance in IR region but thick samples were translucent. In our previous study we show upconversion luminescent properties in thin transparent Sialon ceramics [14]. In this study we focused on thick samples having better IR transparency and luminescent in visible (down conversion) as well as in NIR region for the first time.

Experimental

The composition investigated here was designed according to the formula $\text{Me}_{m/v}\text{Si}_{12-(m+n)}\text{Al}_{m+n}\text{O}_n\text{N}_{16-n}$ [15]. The main composition with Er_2O_3 and Yb_2O_3 co-doped with Er_2O_3 were made, and denoted as SAE (10.92 wt% Er_2O_3) and SAEY (3 wt% Er_2O_3 and 8 wt% Yb_2O_3), respectively. The starting powders used for the composition were α - Si_3N_4 (SN-E10, UBE Co., Japan), Al_2O_3 (High purity chemicals Co. Ltd., Japan), AlN (Grade F, Tokuyama Corp., Japan), Er_2O_3 (High purity chemicals Co. Ltd., Japan) and Yb_2O_3 (High purity chemicals Co. Ltd., Japan). The mixed powders were put into the polyethylene bottle with high purity Si_3N_4 balls in absolute ethanol and milled for 24 hours. After the milling, the mixed slurry was dried at 40 °C in a rotary evaporator and then put into drying oven at

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80 °C for 8 hours. The obtained powder was dry milled with Si_3N_4 balls for 12 hours. Then the powder was sieved through a 150 μm aperture sieve.

The powder was packed into the graphite mould with an inner diameter of 50 mm to make about 2 mm thick sample and transferred into a hot pressing graphite-element furnace (MVHP, Monocerapia Co. Ltd., Korea). Samples were sintered at 1900 °C for 2 hours in nitrogen environment with a pressure of 30 MPa. The heating rate was firstly 20 °C/min from room temperature to 1050 °C and then 10 °C/min to 1900 °C. The cooling rate was 10 °C/min from 1900 °C to 1050 °C, then naturally to room temperature in the furnace. The samples were made 0.8 mm thickness and both side were polished.

The phases of crystalline Sialon ceramics were characterized by X-ray diffractometer (XRD, Cu K α , RIGAKU D/MAX 2200HR diffractometer, Japan). The optical transmittance from 200 nm to 1100 nm was measured by spectrophotometer (MECASYS Optizen2120), 1200-2500 nm by Jasco 570 and 2500-5000 nm by Bruker Vertex 70. The IR emission spectra of specimen excited with 980 nm IR light and supplied by 100-290 mW of a continuous wave laser diode were obtained on the Andor spectrophotometer in transmittance mode.

Results and Discussion

The phases of samples SAE and SAEY were analyzed by XRD patterns after sintering. The main phase was observed as α -Sialon as shown in Fig. 1(a). The silicon in the XRD patterns was added as a standard to calculate the lattice parameters. The lattice parameter values were calculated for SAE ($a = 0.7818$ nm and $b = 0.5701$ nm) and SAEY ($a = 0.7808$ nm and $b = 0.5650$ nm). The lattice parameters were slightly increased in SAE than SAEY due to the insertion of only Er^{3+} cation having large cationic size than that of Yb^{3+} cation.

The α -Sialon is the solid solution of α - Si_3N_4 and is obtained only after stabilized by metal cations. Thus the α -Sialon unit cell consists of maximum two metal cations that compensate the charge discrepancy during the substitution of Si-N by Al-O and Al-N. The crystal structure of α -Sialon is shown in Fig. 1(b). In the structure, the metal cation occupy the interstitial sites and are coordinated by seven (N, O) anions [14]. The α -Sialon phase has hexagonal structure and the $P3_1c$ space group. Thus, the Er^{3+} and Yb^{3+} ions can be inserted into the vacant position at 2b position in the α -Sialon crystal structure. Here, the doping of rare earth oxide is crucial to control the liquid phase and phase transformation [16]. In our previous study [14] on upconversion of Er and Yb doped Sialon ceramics, $m = n = 1.1$ shows better results with good transparency as well as upconversion luminescence. Therefore, we choose the material having $m = n = 1.1$ to observe the IR transparency and luminescence.

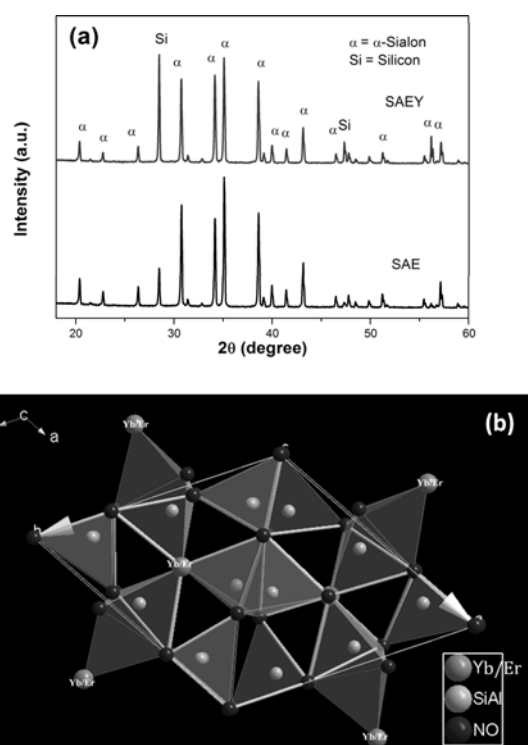


Fig. 1. (a) XRD patterns of SAE and SAEY, (b) the crystal structure of α -Sialon.

The α -Sialon grains are commonly equiaxed in morphology [16]. The large optical band gap and equiaxed grains of α -Sialon make it superior to β -Sialon for optical purposes. The transparency of polycrystalline ceramics is influenced by the pores, grain morphology, phases and grain boundaries [17]. The fabricated Sialon ceramics is not single phase but consists of minor β -Sialon phase, AlN polytypoid and glassy phase. Due to the existence of these different phases degrade the transparency in the Sialon ceramics. The different phases cause the mismatch between the refractive indices and more scattering and absorption of light occurs. The addition of large ions like Er^{3+} or Yb^{3+} in grain boundary phase can increase the refractive index of grain boundary glassy phase than that of small cations [17]. Therefore, higher transmittance was observed in $\text{Er}^{3+}/\text{Yb}^{3+}$ stabilized α -Sialon ceramics. The sample SAE shows higher transmittance in visible region. The SAEY shows higher absorbance around 980 nm as shown in Fig. 2(a) and it is due to the large absorption area of Yb^{3+} at 980 nm and thus Yb^{3+} is used as a sensitizer to sensitize Er^{3+} ion. In another hand, SAEY has almost similar transmittance in both NIR and IR region as shown in Fig. 2(b) and Fig. 2(c), respectively. In Fig. 2(b) the sample SAE shows higher absorbance around 1530 nm. Higher light absorption was observed is due to the 4f-transition of Er^{3+} ions. The absorption peaks at 360 nm, 380 nm, 410 nm, 444 nm, 457 nm, 490 nm, 524 nm, 547 nm, 660 nm, 799 nm and 980 nm correspond to the $^4\text{I}_{15/2} \rightarrow ^4\text{G}_{9/2}$, $^4\text{I}_{15/2} \rightarrow ^4\text{G}_{11/2}$, $^4\text{I}_{15/2} \rightarrow$

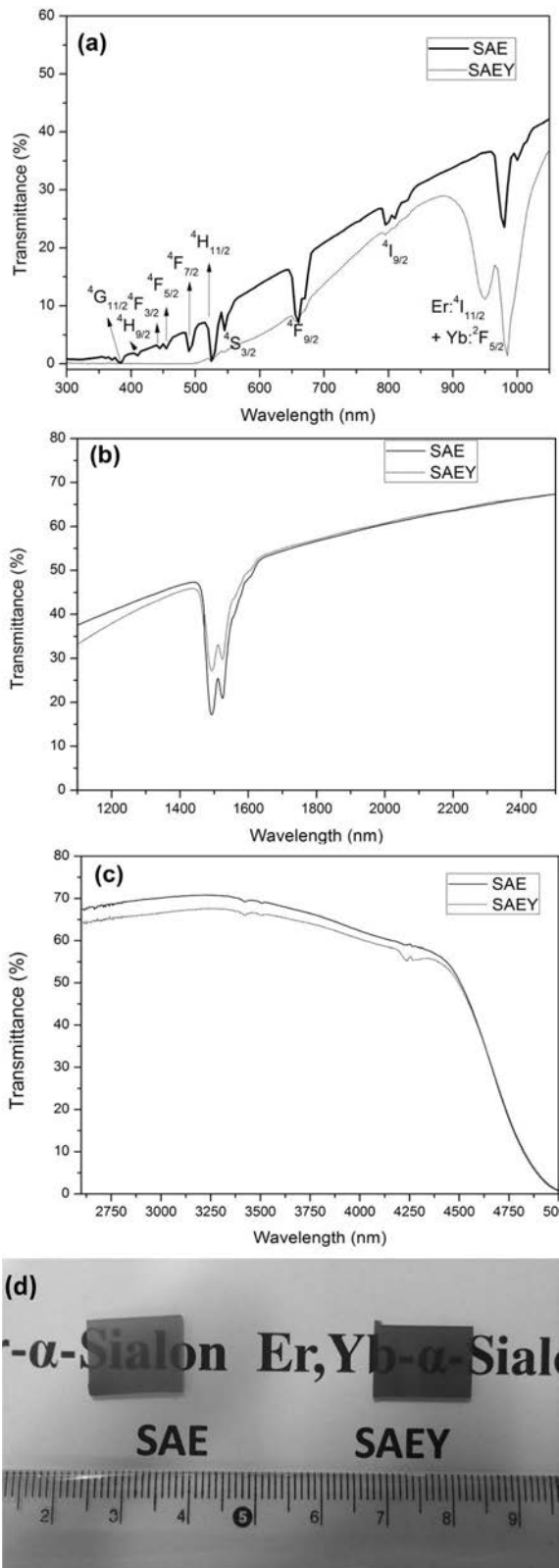


Fig. 2. Transmittance spectra of samples SAE and SAEY: (a) transmittance in visible region, (b) transmittance in NIR region, (c) transmittance in mid IR region, and (d) optical image of sample SAE and SAEY having 0.8 mm thickness.

$^4H_{9/2}$, $^4I_{15/2} \rightarrow ^4F_{3/2}$, $^4I_{15/2} \rightarrow ^4F_{5/2}$, $^4I_{15/2} \rightarrow ^4F_{7/2}$, $^4I_{15/2} \rightarrow ^2H_{11/2}$, $^4I_{15/2} \rightarrow ^4S_{3/2}$, $^4I_{15/2} \rightarrow ^4F_{9/2}$, $^4I_{15/2} \rightarrow ^4I_{9/2}$, and

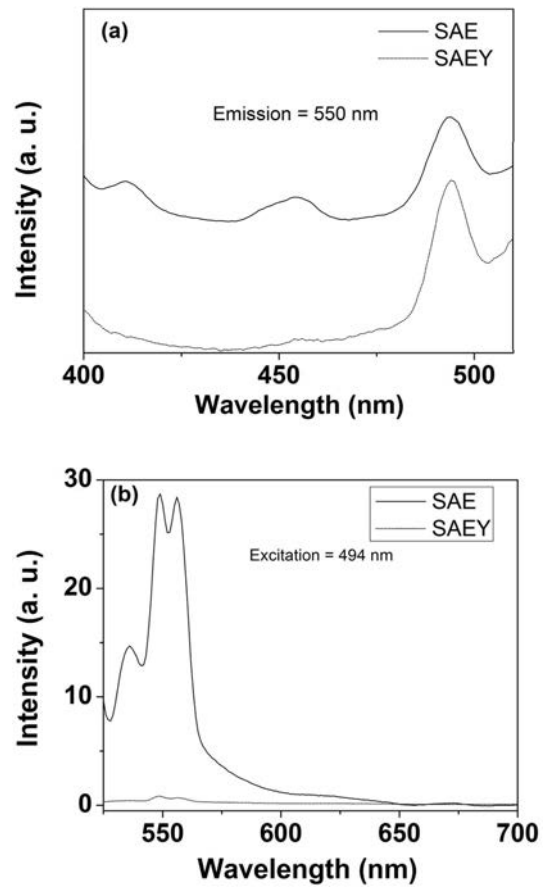


Fig. 3. (a) Excitation spectra of SAE and SAEY, (b) down conversion luminescence spectra excited under 494 nm wavelength for sample SAE and SAEY.

$^4I_{15/2} \rightarrow ^4I_{11/2}$, transition of Er^{3+} ions, respectively. In SAEY, broadening of absorption was found in 980 nm which is due to the $^4F_{7/2} \rightarrow ^4F_{5/2}$ transition of Yb^{3+} ions. The pink and yellow color of the samples shown in Fig. 2(a) are the characteristic color of Er^{3+} and Yb^{3+} ions, respectively.

The down conversion luminescence was observed in green region as excited under 494 nm wavelength as shown in Fig. 3. The luminescence was due to the $^4S_{3/2} \rightarrow ^4I_{15/2}$ transition of Er^{3+} ion. In previous study of upconversion in Sialon ceramics, the main upconversion luminescence was also observed in green region excited under 980 nm wavelength [14]. However, in this study, the green luminescence was due to the down conversion. The sample SAE shows higher luminescence intensity in green region as compared to SAEY. In SAEY, the concentration of Yb^{3+} was higher to Er^{3+} ions and due to low concentration of Er^{3+} ions in Sialon ceramics causes poor luminescence. Here, Yb^{3+} was co-doped as a sensitizer, however, there is no absorption of Yb^{3+} at 494 nm to sensitize the Er^{3+} ion. Thus, Yb^{3+} may be efficient in IR region near 980 nm, where it has higher absorption cross section. Thus, in most of the upconversion studies, Yb^{3+} are co-doped along Er^{3+} ions for better performance [4].

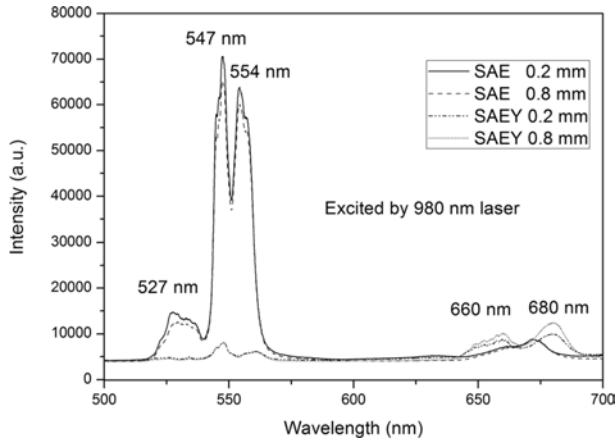


Fig. 4. Upconversion emission spectra of SAE and SAEY having 0.2 and 0.8 mm thickness excited by 980 nm laser diode.

The upconversion process in $\text{Er}^{3+}/\text{Yb}^{3+}$ stabilized α -Sialon has been studied for 0.8 mm thicknesses. In previous study, the upconversion process of thin samples 0.2 mm had been studied in detail [14]. In this study, we analyzed the effect of thickness on upconversion process. In sample SAE, the thickness has no such change in luminescence. However, in SAEY the 0.8 mm thickness sample shows high red upconversion luminescence as shown in Fig. 4. Almost similar green upconversion spectra were observed for SAE and SAEY having different thicknesses. In SAE red luminescence was smaller and intensities and nature of spectra were similar. However, in SAEY, 0.8 thickness sample shows little higher red luminescence. Brown *et al.* [18] reported that thick samples can trapped the radiation more efficiently in spite of low concentration. Therefore, even low concentration of Er^{3+} in SAEY than SAE, the red emission was higher. In other hand, SAE with 0.8 mm thickness shows slightly lower luminescence in green region than 0.2 mm thickness sample. This may be due to the lower transparency of the material in lower wavelength that absorbs more light than in higher wavelength. Also, in polycrystalline ceramics, with increasing the thickness, the transparency of the material decreased.

Since, UC emission in Er - α -Sialon system is due to $4f$ - $4f$ transitions in Er^{3+} ions. There is no significant increase of green luminescence with co-doping of Yb^{3+} . The green upconversion emission in SAE is due to the excited state absorption (ESA) process. Firstly, a 980 nm photon offers the energy to Er^{3+} ion, and it is excited from ground state to $^4\text{I}_{11/2}$ state by ground state absorption (GSA) process. And another 980 nm photon continuously offers energy to Er^{3+} ion and excites it from $^4\text{I}_{11/2}$ state to $^4\text{I}_{7/2}$ state by ESA process. Then, with non-radiative relaxation processes, the excited Er^{3+} ion from $^4\text{I}_{7/2}$ state undergoes to $^2\text{H}_{11/2}$ state or $^4\text{S}_{3/2}$ state, and from these two states results the green emission at 527 nm and 547 nm, respectively. For the red UC emission, population at $^4\text{I}_{11/2}$ state then decays

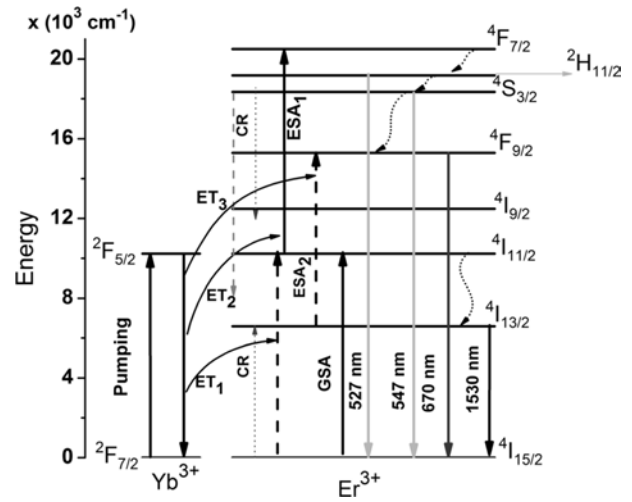


Fig. 5. Schematic energy level diagram of Yb^{3+} and Er^{3+} system showing possible excitation mechanism under 980 nm.

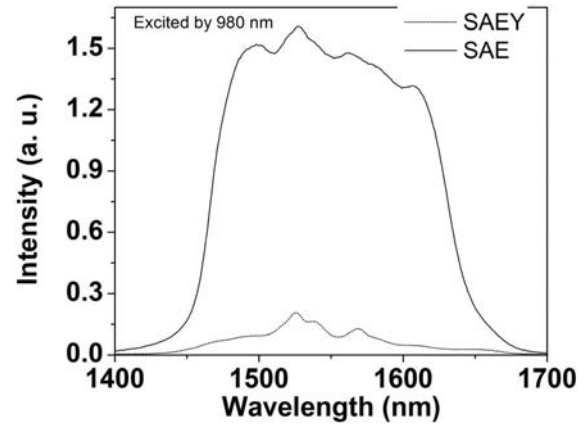


Fig. 6. NIR luminescence spectra of SAE and SAEY under 980 nm excitation (156 mW power).

non-radiatively to the long living $^4\text{I}_{13/2}$ state due to the multi-phonon relaxation process and are then promoted to the $^4\text{F}_{9/2}$ state by one of the following processes: ESA_2 : $^4\text{I}_{13/2} (\text{Er}^{3+}) + \text{a photon} \rightarrow ^4\text{F}_{9/2} (\text{Er}^{3+})$, ET_3 from Yb^{3+} : $^2\text{F}_{5/2} (\text{Yb}^{3+}) + ^4\text{I}_{13/2} (\text{Er}^{3+}) \rightarrow ^2\text{F}_{7/2} (\text{Yb}^{3+}) + ^4\text{F}_{9/2} (\text{Er}^{3+})$, and ET from the $^4\text{I}_{11/2}$ state of adjacent Er^{3+} : $^4\text{I}_{11/2} (\text{Er}^{3+}) + ^4\text{I}_{13/2} (\text{Er}^{3+}) \rightarrow ^4\text{I}_{15/2} (\text{Er}^{3+}) + ^4\text{F}_{9/2} (\text{Er}^{3+})$. The population of $^4\text{F}_{9/2}$ is based on the ET from Yb^{3+} as is confirmed with the strong dependence of the red emission with sensitizer concentration. It is also possible that a non-radiative relaxation from $^2\text{H}_{11/2} + ^4\text{S}_{3/2}$ populates $^4\text{F}_{9/2}$ energy level, because red emission (670 nm) has been observed even without the presence of sensitizer. Thus, the sensitizer, Yb^{3+} in SAEY gives higher red upconversion luminescence as compared to SAE and thus energy transfer upconversion (ETU) process had occurred even the Er^{3+} concentration was lower in SAEY to give red luminescence. The proposed energy transfer model in $\text{Er}^{3+}/\text{Yb}^{3+}$ Sialon system is shown in Fig. 5.

Fig. 6 shows the NIR luminescence of SAE and SAEY

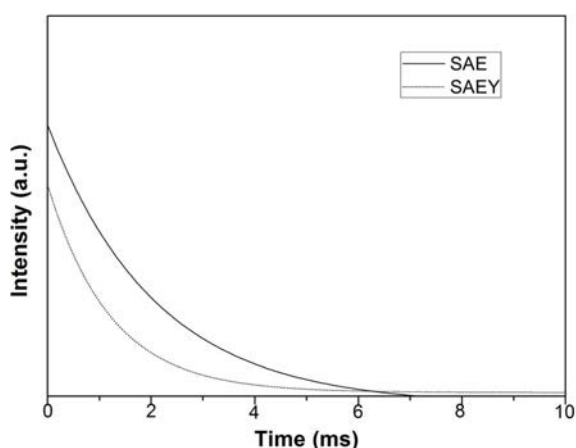


Fig. 7. Decay curves of 1530 nm NIR emission under 980 nm excitation for sample SAE and SAEY.

centered at 1530 nm under 980 nm irradiation. The Er^{3+} ion from the ground state ($^4\text{I}_{15/2}$) is excited to the $^4\text{I}_{11/2}$ state and under goes to $^4\text{I}_{13/2}$ via non-radiative relaxation that results to down-conversion IR luminescence at 1530 nm. The spectral bandwidth of 170 nm was observed for SAE. The NIR emission of SAEY was very low as compared to SAE and main emission for SAEY was also centered at 1530 nm. The luminescence at 1530 nm is dominant in the band and can be chosen for the laser experiment in the future.

The decay curves for SAE and SAEY pumped by 980 nm laser diode are shown in Fig. 7. In the curves there was no such rise in the beginning as reported by Zhou *et al.* [4]. Generally, such rise at initial time of curves was observed due to direct energy transfer from Yb^{3+} ions to Er^{3+} ions. Thus, it shows that in SAEY, no such observable energy transfer was observed. The decay time lowers with addition of Yb^{3+} ions in SAEY as compared to SAE. The lasting times for SAE and SAEY are 2.1 ms and 1.2 ms respectively. Zhou *et al.* [4] also reported that with Yb^{3+} addition, the life time decreases because Yb^{3+} ions can act as acceptors, while Er^{3+} ions as providers during energy transfer process. Therefore, for NIR luminescence, the higher Er^{3+} concentration have higher luminescence life time [1].

Moreover, the Sialon ceramics are known as a structural material having excellent mechanical properties [13]. The fabricated Sialon ceramics shows higher transparency in mid IR region above 70% and can be useful for IR windows and other fields where IR transparency is required in extreme conditions.

Conclusions

The NIR emission, visible down conversion luminescence and upconversion dependence on thickness were analyzed. The co-doping of Yb^{3+} along Er^{3+} shows higher red

upconversion luminescence but lowers the green upconversion luminescence as well as NIR luminescence intensity. The life time at 1530 nm was also analyzed. The sample doped only with Er^{3+} had higher life time than Yb^{3+} co-doped sample. The fabricated Sialon ceramics shows higher IR transmittance than any other Sialon ceramics having 0.8 mm thickness to a date. The fabricated new host material having good transparency may find potential application in NIR.

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