Intense visible and near infrared upconversion in M$_2$O$_2$S: Er (M = Y, Gd, La) phosphor under 1550 nm excitation

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The 1550 nm excited upconversion spectral studies of Yb$^{3+}$ and Er$^{3+}$ co doped M$_2$O$_2$S (M = La, Gd, Y) phosphors were reported for the first time. Studies show that all the compositions are stronger in red emission with the highest intensity in Gd$_2$O$_2$S and lowest in Y$_2$O$_2$S. The red to green emission intensity ratios are 2.7, 3.6 and 3 in Gd$_2$O$_2$S, La$_2$O$_2$S and Y$_2$O$_2$S respectively. Mechanisms of up conversion by multiphoton absorption and energy transfer processes are interpreted and explained.

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1. Introduction
Upconversion is the spectroscopic process where a low energy photon i.e. higher wavelength is converted into one or more high energy photons i.e. lower wavelength. Spectroscopically this is happening through the multiphoton absorption process where a low energy photon is being absorbed to the higher state by multiphoton absorption. In order to have efficient two photon absorption the material should have higher multiphoton absorption coefficient that enables the application of several organic nonlinear materials as potential candidates for efficient upconversion. However, it was found that upconversion can also occur efficiently in several trivalent rare earths doped materials, where the upconversion is mainly happening through multiphoton absorption through real excited states through the process of excited state absorption and other energy transfer processes. Since the upconversion processes take place through the real states, the upconversion emission could be observed even at low excitation laser power and that is an added advantage of rare earth doped upconversion phosphors. At present, rare earth doped upconversion phosphor finds a big market in the Photonics industry. The applications of these phosphors could be found in several areas such as security, solid state lasers [1], IR detection, medical imaging, therapy [2, 3], solid state displays (2D, 3D) [4], and fiber optic amplifiers [5]. The upconversion efficiency and spectral range of the material depend on the suitable selection of the host-dopant combination. Since the absorption energy levels spread over a wide range of the electromagnetic spectrum in trivalent rare earths, very wide spectral excitation and emission is possible. At present, trivalent Er, Ho and Tm are considered as the potential upconvertors for red, green and blue emissions respectively. Though considerable amount of work has been done on this topic in single crystals, limited work has been done in the area of ceramic powder phosphor that shows efficient upconversion.

One of the key requirements for efficient IR to visible upconversion is that the host material possesses a lower phonon spectral mode, which permits halides and heavy metal combination as the best materials for efficient upconversion. However, since many of the halides are air sensitive as well as toxic, which has weakened its large scale industrial applications. Chalcogenides such as S, Se, Te, etc. are also found to be potential candidates for upconversion though the phonon frequency is little higher than halides. Among Chalcogenides, rare earth oxysulfide possesses several excellent properties such as chemical stability, low toxicity and can be easily mass produced at low cost. It has average phonon energies of about 520 cm$^{-1}$ [6]. For example, Y$_2$O$_2$S: Yb$^{3+}$, Er$^{3+}$ is one of the best mass produced commercial upconversion phosphors. It was found that the upconversion brightness of Y$_2$O$_2$S: Yb$^{3+}$, Er$^{3+}$ is 6.5 times greater than that of Y$_2$O$_2$: Yb$^{3+}$, Er$^{3+}$ [7]. Yocom et al. [8] demonstrated that Y$_2$O$_2$: Yb$^{3+}$, Er$^{3+}$ exhibited 82% lighter outputs compared to that of fluoride.

In this work, a solid-state flux fusion method was adopted to prepare fine M$_2$O$_2$S: Yb$^{3+}$, Er$^{3+}$ (M = Y, Gd, La) phosphors of hexagonal phase, having narrow size particle distribution and with high luminescence efficiency. The 1550 nm excited upconversion optical characteristic of oxysulfide, M$_2$O$_2$S (M = Y, Gd, La) phosphors containing 10 mol% of Er$^{3+}$ were reported. To the best our knowledge this is the first report on the 1550 nm excited upconversion studies in oxysulfide phosphors.

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2. Materials and methods

A high temperature solid state flux fusion method was used for the phosphor synthesis. The starting materials are $M_2O_3$, Yb$_2O_3$, Er$_2O_3$, (M = Y, Gd, La, Sigma Aldrich, all 99.999%), S (powder) and flux Na$_2$CO$_3$, K$_2$PO$_4$ (Sigma Aldrich, 99.99%). Both S and Na$_2$CO$_3$ were 30 to 50 wt.% and K$_2$PO$_4$ was 20 wt.% of the total weight. The starting chemicals were thoroughly mixed using agate mortar and then heated in a muffle furnace at 1150 °C for 60 min. The samples were then taken out and washed six times with distilled water and finally with a mild hydrochloric acid. The washed powder was subsequently dried and sieved. X-ray powder diffraction is performed at 40 kV and 30 mA in the parallel beam method using a RIGAKU Altima IV X-ray diffractometer with Cu Kα. More details about the samples preparations, compositions, and particle characterizations are reported in our earlier communication [9]. The upconversion spectra are recorded by the USB2000 Ocean optics spectrometer with a power tunable 1550 nm Fabry Perot laser diode (ThorLab, Model LM1452) and optical fiber. Upconversion efficiency on dry powder was measured using an integrating sphere. For comparison all measurements were done under identical conditions.

3. Results and discussions

A typical XRD pattern obtained for the La$_2$O$_2$S: Yb$^{3+}$, Er$^{3+}$ (LOS) was shown in Fig. 1. The peak positions are exactly matching with the hexagonal phase of oxysulfide (JCPDS Card No. 26-1422). The XRD results reveal that the well-crystallized La$_2$O$_2$S: Yb$^{3+}$, Er$^{3+}$ sample is in hexagonal structure with lattice parameters $a = b = 0.3852$ nm, $c = 0.6567$ nm and this has also been confirmed from SEM measurements [9].

Crystal structure of La$_2$O$_2$S is shown in Fig. 2. The symmetry is trigonal and the space group is $P6_3/m$. There is one formula unit per unit cell. The structure is very closely related to the A-type rare-earth oxide structure, the difference being that one of the three oxygen sites is occupied by a sulfur atom. Atom positions in La$_2$O$_2$S using lattice vector units are $u = (1/3, 2/3, u)$ for two metal atoms with $v = 0.28, ±(1/3, 2/3, v)$ for two oxygen atoms with $v = 0.63$, and $(0, 0, 0)$ for a sulfur atom. Each metal atom seems to be bonded to four oxygen atoms and three sulfur atoms, to form a seven coordinated geometry with the oxygen and the metal in the same plane.

Fig. 3 shows a 1550 nm excited upconversion in La$_2$O$_2$S: Er$^{3+}$ (10) [LOS] in comparison with Gd$_2$O$_2$S: 10% Er$^{3+}$ [GOS] and Y$_2$O$_2$S: 10% Er$^{3+}$ [YOS]. All samples show four emission bands centered at 553, 670, 820, 983 nm. The fluorescence branching ratios obtained for these four bands are respectively 9.2, 27.5, 9, 51.4% (YOS), 7, 29, 13, 49.7% (LOS) and 12, 42, 10, 35.8% (GOS). The total upconversion efficiency in these phosphors is measured to be 3.5, 2.0 and 1.6% respectively in GOS, LOS and YOS. The green, red and NIR emission band efficiencies are respectively 0.42, 1.47, 1.23% (GOS), 0.14, 0.58, 0.99% (LOS) and 0.147, 0.44, 0.88% (YOS). Thus, in terms of the upconversion efficiency, the Gd$_2$O$_2$S: 10% Er$^{3+}$ composition is the most efficient and Y$_2$O$_2$S: 10% Er$^{3+}$ is the least efficient. The inset of Fig. 3 shows the photon count distributions of the three compositions for all emissions bands. It is interesting to note that under 980 nm excitation, these compositions show brighter green emission (Fig. 4) due to two photon induced upconversion processes [9]. This shows that the upconversion processes in these compositions are wavelength dependent. In all samples, the upconversion emission is so intense that even with a few mW excitation power the emission can be seen with naked eye. Because of the extreme brightness of the emission, 20 mW of excitation power was used for all experiments to avoid the saturation in the spectrometer. The inset of Fig. 3 shows a photograph of the green upconversion emission in La$_2$O$_2$S: 10% Er$^{3+}$ under 20 mW excitation at 1550 nm. Though the 980 nm excited upconversion mechanisms in Er$^{3+}$ and Er$^{3+}$/Yb$^{3+}$ system was well studied in several materials [10,11], only limited number of work [12] has been reported on the 1550 nm excited upconversion. The emission mechanisms are briefly explained using the following energy level diagram drawn to scale as shown in Fig. 5. Emission bands observed at 553, 670, 820, 983 nm are assigned to the $^4H_{11/2} \rightarrow ^4I_{15/2}$, $^2S_{1/2} \rightarrow ^4I_{15/2}$, $^4I_{9/2} \rightarrow ^4I_{15/2}$ and $^4I_{9/2} \rightarrow ^4I_{15/2}$ transitions respectively. The appearance of both green and red emission bands can be explained on the basis of various processes such as three photon absorption (TPA) and excited state absorption (ESA). TPA is a nonlinear process where the visible photons are created by the simultaneous absorption of three photons and mediated through a real or virtual intermediate level. TPA is relevant when excitation light sources being used have high power that is sufficient enough to create virtual intermediate levels in materials with high TPA cross section. In the case of trivalent Er$^{3+}$, TPA can occur through the real states because of the presence of such matching energy levels. When the $^4I_{13/2}$ level is excited by 1550 nm photons, part of the excitation energy is radiatively relaxed through the emission channel $^4I_{13/2} \rightarrow ^4I_{15/2}$ as 1550 nm emission. At the same time, the populated $^4I_{11/2}$ level is excited to the $^4I_{13/2}$ level by the absorption of a second photon. From $^4I_{9/2}$ level another 1550 nm photon can be absorbed to an equally similar excited level $^4I_{13/2}$. These excited state processes can equally happen due to
excited state absorption (ESA) processes because of the matching excited energy levels. After these excited state processes, de-excitation accumulates electron in different excited states and the intensity of emission depends on the electron density at that particular level as well as the non-radiative contribution to the emission band. Since the $^2H_{11/2}$ level couples to the $^2S_{3/2}$ level by lattice phonon relaxation between closely spaced energy levels, the level $^2S_{3/2}$ act like a metastable level and the emission from $^2S_{3/2}$ to $^4I_{15/2}$ results in 553 nm emission. Fractional populations accumulated in levels $^4F_{9/2}$ $\leftrightarrow$ $^4I_{9/2}$ and $^4I_{11/2}$ decays to $^4I_{15/2}$ giving rise to emissions at 670, 820 and 985 nm respectively. In oxysulfide host because of the weak lattice phonon relaxation, the non radiative contribution to 553, 670, 820 and 985 nm emission bands from the energy gap between $^2S_{3/2}$ $\leftrightarrow$ $^4F_{9/2}$ (emission at 3.16 $\mu$m), $^4F_{9/2}$ $\leftrightarrow$ $^4I_{9/2}$ (emission at 3.16 $\mu$m), $^4I_{9/2}$ $\leftrightarrow$ $^4I_{13/2}$($^{3+}$), $^4I_{15/2}$($^{3+}$) $\rightarrow$ $^4I_{11/2}$($^{3+}$) $\rightarrow$ $^4I_{15/2}$($^{3+}$) $\rightarrow$ $^4I_{13/2}$($^{3+}$). An increase in $^{3+}$ concentration enforces these cross relaxation processes and that would influence mainly the 553 and 820 nm emissions.

4. Conclusion

We have studied the 1550 nm excited upconversion processes in $^{3+}$ doped $M_2O_2S$ ($M=Y$, Gd, La). The upconversion mechanisms were interpreted as a result of three photon absorption, excited state absorption and cross relaxation from energy transfer process. The upconversion process in these phosphors is found to be wavelength dependent. The upconversion efficiency in this material is so high that even with low excitation power; one can see the green
upconversion with the naked eye. The low power excitation upconversion mechanism in this material offers several potential applications such as solar energy conversion and low threshold upconversion lasers.

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Fig. 6. Functional dependence of the excitation power vs. emission intensity of the observed emission bands under 1550 nm excitation.

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