University of Texas Rio Grande Valley

ScholarWorks @ UTRGV

Physics and Astronomy Faculty Publications
and Presentations

College of Sciences

5-2012

Synthesis and Upconversion Spectroscopy of Yb Er Doped M₂O₂S (M = La, Gd, Y) Phosphors

G. A. Kumar

University of Texas at San Antonio

Madhab Pokhrel

The University of Texas Rio Grande Valley

Dhiraj K. Sardar

Alejandrina Martinez

Follow this and additional works at: https://scholarworks.utrgv.edu/pa_fac

Part of the [Astrophysics and Astronomy Commons](#), and the [Physics Commons](#)

Recommended Citation

Kumar, G. A., et al. "Synthesis and Upconversion Spectroscopy of Yb Er Doped M₂O₂S (M = La, Gd, Y) Phosphors." *Science of Advanced Materials*, vol. 4, no. 5–6, May 2012, pp. 623–30, doi:10.1166/sam.2012.1329.

This Article is brought to you for free and open access by the College of Sciences at ScholarWorks @ UTRGV. It has been accepted for inclusion in Physics and Astronomy Faculty Publications and Presentations by an authorized administrator of ScholarWorks @ UTRGV. For more information, please contact justin.white@utrgv.edu, william.flores01@utrgv.edu.

Synthesis and Upconversion Spectroscopy of Yb Er Doped M_2O_2S ($M = La, Gd, Y$) Phosphors

G. A. Kumar^{1,*}, Madhab Pokhrel¹, Alejandrina Martinez², and D. K. Sardar¹

¹Department of Physics and Astronomy, University of Texas at San Antonio, San Antonio, Texas 78249, USA

²Centro De Investigaciones En Optica, Leon Gto, Mexico 37150

ABSTRACT

Yb and Er doped M_2O_2S ($M = Y, Gd, La$) phosphor was synthesized by solid state flux fusion method and their up conversion spectral properties were studied as a function different Yb concentrations. The solid state flux fusion results in well crystallized hexagonal shaped phosphor particles of average size 4–6 μm . Upconversion spectral studies shows that all the compositions are stronger in green emission with the green emission intensity 1.7 times than the red in composition $Gd_2O_2S:Yb(8)Er(1)$, $Y_2O_2S:Yb(9)Er(1)$, $La_2O_2S:Yb(3)Er(7)$ (All mol%). The internal upconversion efficiency for the green emission bands was calculated to be 74, 62, 100% respectively in $Gd_2O_2S:Yb(8)Er(1)$, $Y_2O_2S:Yb(8)Er(1)$, $La_2O_2S:Yb(8)Er(1)$. Mechanisms of up conversion by two photon and energy transfer processes are interpreted and explained. The x, y color coordinates are measured and the color tunability was analyzed as a function of the 980 nm excitation power. Results shows that all phosphor offers power dependent color tuning properties where the emission color can be tuned from 490 nm to 550 nm by simply changing the 980 nm excitation power from 10–50 mW.

KEYWORDS: Upconversion, Phosphor, Two Photon Absorption, Energy Transfer, Energy Conversion.

1. INTRODUCTION

Up conversion is the spectroscopic process where a low energy photon of higher wavelength is converted into one or more high energy photons of 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 and that enables the application of several organic nonlinear materials as potential candidates for efficient up conversion. However, it was found that up conversion can also occur efficiently in several trivalent rare earth doped materials. Here the up conversion is mainly happening through multiphoton absorption through real excited states through the process of excited state absorption and other energy transfer processes. Since the processes is happening through the real states the up conversion emission could be observed even at low excitation laser power and that is an added advantage of rare earth doped up conversion phosphors. At present rare earth doped up conversion phosphor find a big market in the Photonics industry. The application of these phosphors could found in several areas

such as security, solid state lasers.¹ IR detection, medical imaging, therapy,^{2,3} solid state displays (2D, 3D),⁴ fiber optic amplifiers.⁵ The up conversion efficiency and spectral range of the material depends on the suitable selection of the host-dopant combination. In trivalent rare earths since the absorption energy levels spread over a wide range of the electromagnetic spectrum 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 emission. Though considerable amount of work has been done on this topic in single crystals only 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 up conversion is that the host material possess a low phonon spectral mode which permits halides and heavy metal combination as the best materials for efficient up conversion. However, since many of the halides are air sensitive as well as toxic many of them could not find large scale industrial applications. Chalcogenides such as S, Se, Te, etc. are also found to be potential candidates for up conversion 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, $Y_2O_2S: Yb, Er$ is one of the best mass produced commercial up conversion phosphors.

*Author to whom correspondence should be addressed.

Email: mail-akgsh@yahoo.com

Received: 1 September 2011

Accepted: 26 September 2011

It was found that the upconversion brightness of $Y_2O_2S: Yb, Er$ is 6.5 times to that of $Y_2O_3: Yb, Er$.⁷ Yocom et al.⁸ demonstrated that $Y_2O_2S: Yb, Er$ exhibited 82% light outputs to that of fluoride. In this work, a solid-state flux fusion method was adopted to prepare fine $M_2O_2S: Yb, Er$ ($M = Y, Gd, La$) phosphors with hexagonal shape, narrow size distribution and high luminescence efficiency. The up conversion optical characteristic of green emitter phosphors are investigated for wide range of dopant compositions and optimum compositions have been explored for the highest light output.

Crystal structure of La_2O_2S is shown in Figure 1. The symmetry is trigonal and the space group is $P\bar{3}m1$. 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_2O_2S using lattice vector units are $\pm(1/3, 2/3, u)$ for two metal atoms with $u \sim 0.28$, $\pm(1/3, 2/3, v)$ for two oxygen atoms with $v \sim 0.63$, 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.

2. EXPERIMENTAL DETAILS

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_2CO_3 , K_3PO_4 (Sigma Aldrich, 99.99%). Two different sets of samples were prepared with different Yb: Er ratio. In the first series the total Yb+Er molar ratio was fixed at 10 mol% viz. (0:10),

Fig. 1. Crystal structure of La_2O_2S showing the location of La (Pink), O (red) and S (yellow) atoms. Both La and O are in the same plane.

(1:9), (2:8), (3:7), (5:5), (9:1), (9.5:0.5). In the second set the Er concentration was kept constant at 1 mol% while Yb was varied and the Yb: Er ratios were viz. (0:1), (1:1), (2:1), (3:1), (5:1), (9:1), (8:1). Both S and Na_2CO_3 were 30 to 50 wt% and K_3PO_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. When the furnace was cooled down the samples were taken out and washed with distilled water 6 times and finally with a mild hydrochloric acid. The washed powder was subsequently dried and sieved. The particle size is analyzed by Coulter LS230 light scattering particle size analyzer. 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 $K\alpha$. The morphology of the samples was observed using a Hitachi S5500 field emission scanning transmission electron microscope (FE-STEM) operated at 30 kV in secondary electron mode. The up conversion spectra are recorded by the USB2000 Ocean optics spectrometer with a power tunable 980 nm laser diode (BW Tek 980) and optical fiber. For comparison all samples were equally weighed and packed in cuvettes and excited with 20 mW of laser power. For CIE color coordinates measurements the spectrometer was used in the emissive color mode at 2 degree observer angle.

3. RESULTS AND DISCUSSION

3.1. Phase and Morphology

A typical XRD pattern obtained for the $La_2O_2S: YbEr$ (LOS) was shown in Figure 2. The peak positions are exactly matching with the hexagonal phase of oxy sulphide (JCPDS Card No. 26-1422). The XRD results reveal that the well-crystallized $La_2O_2S: Yb, Er$ sample is in hexagonal structure with cell parameters $a = b = 0.3852$ nm, $c = 0.6567$ nm. According to the dynamic light scattering measurements (Fig. 3) the average particle size was estimated

Fig. 2. XRD pattern of the $La_2O_2S: YbEr$ sample.

Fig. 3. Particle size distribution from dynamic light scattering measurements.

to be $6.176 \mu\text{m}$ with a FWHM of $13.6 \mu\text{m}$. SEM micrograph obtained from different locations shows that the material mostly crystallized in hexagonal shape with mean particle length $6.66 \pm 0.58 \mu\text{m}$ and width $2.67 \pm 0.1 \mu\text{m}$. For $Y_2O_2S: YbEr$ (YOS) and $Gd_2O_2S: YbEr$ (GOS) the average particle size obtained from light scattering measurements are respectively $3.8 \mu\text{m}$ (FWHM of $4.9 \mu\text{m}$) and $6.15 \mu\text{m}$ (FWHM of $8.9 \mu\text{m}$). A typical SEM micrograph of the $La_2O_2S: YbEr$ sample is shown in Figure 4(c) in comparison with the SEM images of $Gd_2O_2S: YbEr$ and $Y_2O_2S: YbEr$. SEM images show that the average size and particle morphology almost remains the same in $Y_2O_2S: YbEr$ and $La_2O_2S: YbEr$ whereas in $Gd_2O_2S: YbEr$ several particles are rod-like. It should be noted that the primary particle size of M_2O_3 was reduced from $10 \mu\text{m}$ to $3.8 \mu\text{m}$ by flux fusion method. SEM micrograph obtained from different locations shows that the material mostly crystallized in hexagonal shape. Analysis of the elemental composition by EDS shows the wt% of various elements inside the composition $M_2O_2S: Yb$ (2) Er (1) as $M = 42.5\%$, $Yb = 2.53\%$, $Er = 1.05\%$ and $S = 7.46\%$ which is almost in agreement with the starting composition $M = 42.2\%$, $Yb = 2.3\%$ and $Er = 0.74\%$.

The growth mechanism of M_2O_2S phosphor in flux fusion process is well understood.⁹ The formation of M_2O_2S phosphor particle follows the chemical formula

The oxysulphide particles are grown on the M_2O_2 nuclei through the sulfurization process on the M_2O_3 by the molten Na_2S_x flux and the process was shown in Figure 5.

Fig. 4. SEM micrograph of oxysulphide phosphor powder prepared by the flux fusion method; (a) $Gd_2O_2S: YbEr$ (b) $Y_2O_2S: YbEr$ (c) $La_2O_2S: YbEr$.

Since the M_2O_3 particles are dissolved in the molten Na_2S_x flux the original precursor M_2O_3 particle size and distribution are not maintained and the dissolved particle grow into M_2O_2S particle. Assuming the solubility and mobility of the M_2O_2S in the Na_2S_x flux solution are very small, the dissolution of M_2O_3 , subsequent nucleation and growth of M_2O_2S seed crystal may be restricted to a small volume covering one particle. As the temperature increases, all of the M_2O_3 particles dissolve suddenly in a volume V_1 of the flux converting them into M_2O_2S . If the solubility of M_2O_2S in the flux solution is less, the flux solution the region V_1 is quickly saturated instantly with M_2O_2S and this leads formation of the first M_2O_2S nucleation in this

Fig. 5. Crystal growth mechanism of M_2O_2S phosphor. $M = Gd, Y, La$.

saturated solution. As the flux temperature increases few M_2O_2S particles are dissolved in the molten flux solution of volume V_2 ($V_2 > V_1$) and thereby creating a saturated region of M_2O_2S in volume V_2 and the process continues to different flux volume thereby increasing the size of the M_2O_2S particles. The rate of particle growth is given by

$$\frac{d\phi}{dt} = A \exp\left(\frac{-\Delta E}{kT}\right) \quad (1)$$

Where A is a constant for a particular flux, k the Boltzmann constant, T the temperature in K and E is the activation energy. The particle size and shape thus depends on various factors such as the firing temperature, time and type of fluxes.¹⁰

3.2. Upconversion

Figure 6 shows a 980 nm excited upconversion in La_2O_2S : Yb (3) Er (7) in comparison with Gd_2O_2S : Yb(8)Er(1) and Y_2O_2S :Yb(9):Er(1).^a As usual all samples show green and red emissions. The fluorescence branching ratios of the green and red up conversion bands are respectively 48.5% and 38.8%. In the case of YOS and GOS they are respectively 49.5% (G), 48.3% (R) and 56.7% (G), 43.2% (R). However the G/R intensity ratios in GOS, YOS and LOS are respectively 1.31, 2.01 and 2.05. In all samples the up conversion in these samples are so intense that even with $<15 \mu W$ excitation the emission can be seen with naked eye. Further, the emission could be recorded with $700 \mu W$ excitation power. Because of the extreme brightness of the emission nearly 20 mW of excitation power was used in all experiments. The inset of Figure 5(b) shows a photograph of the green upconversion emission under 20 mW excitation at 980 nm.

The up conversion process in Yb Er system is well understood in several materials^{11,12} and is briefly explained in the following energy level diagram shown in Figure 7. Emission bands were observed at 410 nm, 492 nm, 533 nm, 549 nm, 669.8 nm and 822 nm and are assigned to the $^2H_{9/2} \rightarrow ^4I_{15/2}$, $^4F_{7/2} \rightarrow ^4I_{15/2}$, $^2H_{11/2} \rightarrow ^4I_{15/2}$, $^4S_{3/2} \rightarrow ^4I_{15/2}$, $^4F_{9/2} \rightarrow ^4I_{15/2}$ and $^4I_{9/2} \rightarrow ^4I_{15/2}$ transitions respectively. The appearance of both the blue, green and red emission bands can be explained on the basis of various processes such as two photon absorption (TPA), excited

Fig. 6. Upconversion emission spectrum of the oxysulphide phosphor under 980 nm laser excitation with 20 mW excitation power.

state absorption (ESA) and energy transfer (ET). TPA is a nonlinear process where the visible photons are created by the simultaneous absorption of two 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 $^4I_{11/2}$ level is excited by 980 nm directly through Er^{3+} or through Yb^{3+} excitation photons, part of the excitation energy at the $^4I_{11/2}$ level relaxes non-radiatively to the $^4I_{13/2}$ level giving rise to the $^4I_{13/2} \rightarrow ^4I_{15/2}$ emission. At the same time, the populated $^4I_{11/2}$ level is excited to the $^4F_{7/2}$ state by ESA of a second photon. From $^4F_{7/2}$ level

Fig. 7. Energy level diagram of Yb Er system showing possible excitation and de excitation mechanism under 980 nm. MPA-Multiphoton absorption; ET-Energy Transfer.

^aCompositions based on highest emission intensity.

Fig. 8. Dependence of the excitation power on the emission intensity of green and red emission.

another 980 nm photon can be absorbed to an equally similar excited level. As explained earlier these excited state processes can equally happen under high photon density through nonlinear absorption processes such as two photon or three photon absorption. 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. The population accumulated in level $^2H_{9/2}$ gives the 410 nm emission by radiatively decaying to $^4I_{15/2}$. Since the efficiency of this third order process is less the emission intensity if the 410 nm band is comparatively weak. On the other hand, the two photon processes that populate the $^4F_{7/2}$ level is so efficient that it can give very efficient green emission transition from $^2H_{11/2}$ due to the fast multiphonon non-radiative decay of $^4F_{7/2}$ level to $^2H_{11/2}$. Because of several closely spaced levels in between $^2H_{11/2}$ and $^4S_{3/2}$ multiphonon relaxation results in decaying the $^2H_{11/2}$ level to $^4S_{3/2}$ yielding the strongest emission band at 549 nm. The decay time of the $^4S_{3/2}$ level is measured to be 295 μs which is sufficient to make this as a meta stable level for the green emission. Further, since the energy gap between $^4S_{3/2}$ and $^4F_{9/2}$ is 2800 cm^{-1} multiphonon relaxation is unlikely to happen and hence the $^4S_{3/2} \rightarrow ^4F_{9/2}$ transition could be radiative.^b Part of the population decaying to level $^4F_{9/2}$ can result in the red emission at 669.8 nm through the $^4F_{9/2} \rightarrow ^4I_{15/2}$ transition. Finally fractional population accumulated in $^4I_{9/2}$ level give rise to the 822 nm emission through $^4I_{9/2} \rightarrow ^4I_{15/2}$ transition. The major process that populate the $^4F_{9/2}$ level of Er^{3+} is the energy transfer process from Yb according to the equation $^2F_{5/2}(Yb^{3+}) + ^4I_{13/2}(Er^{3+}) \rightarrow ^2F_{7/2}(Yb^{3+}) + ^4F_{9/2}(Er^{3+})$.

In order to establish the presence of these non linear processes, the pump power dependence of the emission

bands on the emission intensity was measured and the relationship obtained is plotted in Figure 8. The slope obtained for 533, 549 and 669.8 nm emission bands are respectively 1.38, 1.45 and 1.41 which show that two photon processes contribute to these emissions. It is interesting to note that the present material shows upconversion under 980 nm

Fig. 9. Variation of Green and Red emission intensity as a function of Yb concentration at fixed Er concentration at 1 mol%. (a) $Gd_2O_2S: YbEr$ (b) $Y_2O_2S: YbEr$ (c) $La_2O_2S: YbEr$.

^bWe observed 3.2 μm emission through the $^4S_{3/2} \rightarrow ^4F_{9/2}$ transition.

Fig. 10. Variation of Green and Red emission intensity as a function of Yb concentration at fixed Er + Yb concentration at 10 mol%. (a) $Gd_2O_2S: YbEr$ (b) $Y_2O_2S: YbEr$ (c) $La_2O_2S: YbEr$.

excitation from Xe lamp; this corroborates the fact that in this composition ESA also contributes to the upconversion process. The fact that the material shows intense upconversion under low power excitation shows that the efficiency of upconversion in this material is comparatively higher. Further, under high power excitation the material shows almost linear or saturation in intensity which is probably due to the excitation population saturation at high excitation power.

In order to understand the functional dependence of the red and green emission intensity on the Yb concentrations, two sets of samples were prepared: in the first set the Yb:Er concentration was kept fixed at 10 mol% by proportionally changing Yb and Er concentrations. In the second set the Yb concentration was varied from 0 to 9 mol% by keeping the Er constant at 1 mol%. Results of both experiments are presented in Figures 9(a)–(c) and 10(a)–(c) for GOS, YOS and LOS. The green and red emission intensity variations in these two experimental are entirely different in each of the material. In the first sets of experiments with Er 1 mol% both green and red emission intensity peaks at 7 mol% of Yb in GOS and LOS whereas in YOS up to 9 mol% of Yb both emission intensity goes on increasing. On comparing the three hosts the green emission is more intense in GOS followed by LOS and YOS. In the second sets of experiments with Er + Yb = 10 mol% both green and red emission intensity decreases at 7 mol%, 8 mol%, 4 mol% of Yb respectively in GOS, YOS and LOS. In LOS after 8 mol% of Yb the emission again seems to increase. Comparison of the green emission intensity shows that LOS is the brightest.

The internal quantum efficiency, (η_{int}) of the upconversion band can be evaluated from the ratio of the fluorescence to radiative decay time.¹³ Fluorescence decay curves obtained for the 555 nm emission band are shown in Figure 11. The fluorescence lifetime obtained for the 555 nm emissions are respectively 260, 163 μs

Fig. 11. Fluorescence decay curve of the green emission band in GOS, YOS and LOS at 8 mol% Yb and 1 mol% Er dopant concentrations.

Table I. CIE (x, y, z), (X, Y, Z) color coordinates, color temperature (CCT) and color purity of $La_2O_2S:Yb(8)Er(1)$ for different excitation power.

Power (mW)	Dominant color (nm)	X	Y	Z	x	y	z	CCT (K)	Purity
12	498.7	131.56	185.12	123.19	0.2991	0.4209	0.2801	6531	0.347
18	512.2	696.74	1040.56	263.08	0.3483	0.5202	0.1315	5222	0.265
24	546.6	2072.6	3139.92	422.96	0.3678	0.5572	0.0751	5396	0.508
30	554.4	2998.93	4313.3	610.47	0.3785	0.5444	0.0771	4730	0.488
40	548.8	3374.53	4794.12	797.99	0.3763	0.5347	0.0890	4754	0.412
50	549.4	3749.87	4993.62	954.72	0.3867	0.5149	0.0984	4516	0.343
60	539.0	3782.79	5065.88	1112.18	0.3798	0.5086	0.1117	4620	0.274
70	529.5	3818.79	5136.44	1282.41	0.3730	0.5017	0.1253	4725	0.226
78	516.5	3852.75	5217.82	1443.44	0.3664	0.4963	0.1373	4836	0.212
80	510.9	3886.87	5285.49	1607.49	0.3606	0.4903	0.1491	4940	0.211
96	514.3	3927.62	5372.60	1798.01	0.3539	0.4841	0.1620	5064	0.218
102	506.0	3957.34	5444.54	1932.67	0.3491	0.4804	0.1705	5159	0.226
114	508.1	4002.02	5573.90	2136.71	0.3417	0.4759	0.1824	5317	0.241
126	500.1	4042.70	5640.49	2339.50	0.3363	0.4692	0.1946	5436	0.251

and 295 in $Gd_2O_2S:Yb(8)Er(1)$, $Y_2O_2S:Yb(8)Er(1)$, $La_2O_2S:Yb(8)Er(1)$. Following Judd-Ofelt^{14,15} model we calculated radiative decay times of 353, 264 and 295 μs and this yield an internal quantum yield of 74, 61.7 and 100% in GOS, YOS and LOS.

The excitation saturation at comparatively low power excitation is particularly useful in several Photonics applications such as solar energy converter or laser amplifier where high power excitation was required to achieve the desired energy conversion. With comparatively low power excitation efficient upconversion phosphor layers it would be possible to enhance the energy conversion efficiency of the Si solar cells. The same concept applies to the development of low pump threshold solid state lasers, ceramic lasers and fiber amplifiers created with similar phosphor compositions. As a continuation of this work we are in the process of measuring the external quantum efficiency of the 980/1550 nm to visible and NIR upconversion efficiency in these materials as a function of the compositions with the intension of using them our current solar cell project.

3.3. CIE Color Coordinates Analysis

To measure the color of the visible emission that the human eye perceives, the Commission *internationale de l'éclairage* (CIE) coordinates (x, y, z) were calculated from the (X, Y, Z) tristimulus values as follows¹⁶

$$x = \frac{X}{(X + Y + Z)}, y = \frac{Y}{(X + Y + Z)}, z = \frac{Z}{(X + Y + Z)} \quad (2)$$

where the X, Y , and Z are related to the spectral power distribution function $P(\lambda)$ as

$$X = \int P(\lambda) \bar{x}(\lambda) d\lambda, Y = \int P(\lambda) \bar{y}(\lambda) d\lambda, Z = \int P(\lambda) \bar{z}(\lambda) d\lambda \quad (3)$$

where is the equivalent wavelength of the monochromatic light and $\bar{x}, \bar{y}, \bar{z}$ are color matching functions.

In addition, using the color coordinates calculated above, the correlated color temperatures (CCT) of the mixed upconversion fluorescence corresponding to different excitation powers were given by the McCamy empirical formula¹⁷

$$CCT = -437n^3 + 3601n^2 - 6861n + 5514.31 \quad (4)$$

where $n = (x - x_e)/(y - y_e)$ is the inverse slope line, and $x_e = 0.3320$ and $y_e = 0.1858$. The color coordinates and CCT under different excitation powers are listed in Table I, and the color coordinates are marked in Figure 12 for the brightest compositions in YOS, GOS and LOS. The (x, y) coordinates obtained for YOS, GOS and LOS are respectively (0.3541, 0.5591), (0.3678, 0.5507) and

Fig. 12. CIE color coordinate plot showing the x, y coordinates of the emission in $M_2O_2S:Yb(8)Er(1)$ ($M = Y, Gd$ and La). The emission color was marked by the white arrow.

Fig. 13. Power dependent emission color tuning in oxysulphide phosphor.

(0.3867, 0.5149). It was found that the nature of power dependence of both x and y coordinates are almost the same in all the 3 hosts.

The color tuning range of the three phosphors are shown in Figure 13 where it can be seen that the emission color can be easily tuned from 490 nm to 550 nm by changing the excitation power from 10–50 mW. The curve shows that LOS is sharper in green compared to GOS and YOS.

The color power dependent color tuning possibility of the present phosphor material could find variety of applications such as tunable upconversion ceramic lasers, color tunable phosphor coatings, multicolor biomedical imaging, 3D display, infrared activated LED design as well as in polymer fiber lasers and planar waveguides. Recently we successfully made nanoparticles of several oxysulphide upconversion phosphors and currently investigating the optical properties of these nanoparticles in several fluoropolymers with the intension of making optical fibers and planar waveguide structures for low pump threshold upconversion laser applications.

4. CONCLUSIONS

Using the solid state flux fusion method hexagonal shaped Yb Er doped M_2O_2S ($M = Y, Gd, La$) phosphors were synthesized and its upconversion spectroscopic properties were studied for range of Yb and Er dopant concentrations. Analysis shows that all the compositions are stronger in green emission with the green emission intensity 2 times stronger than the red in composition $Gd_2O_2S:Yb(8)Er(1)$,

$Y_2O_2S:Yb(9)Er(1)$, $La_2O_2S:Yb(3)Er(7)$ (All mol%). The upconversion efficiency in this material is so high that even with less than a 15 μW of 980 nm excitation one could see the green upconversion with naked eye. The internal quantum efficiency obtained for the green emission was 74, 62, 100% respectively for the GOS, YOS and LOT phosphor. The low power excitation upconversion mechanism in this material offers several potential applications such as solar energy conversion and low threshold upconversion lasers. Further, the material offers power dependent color tuning properties where the emission color can be tuned from 490 nm to 550 nm by simply changing the 980 nm excitation power from 10–50 mW. Upconversion color tunability by changing the pump power intensity offers several diverse Photonics applications such as novel three-dimensional solid-state display, upconversion LED lighting, biomedical multi-color imaging, lasers etc.

Acknowledgments: This work was supported by the National Science Foundation Partnerships for Research and Education in Materials (PREM) Grant No. DMR-0934218. Authors are thankful to R. C. Dennis for the assistance in SEM imaging.

References and Notes

1. L. F. Johnson and H. Guggenheim, *Appl. Phys. Lett.* 19, 44 (1971).
2. S. F. Lim, R. Riehn, W. S. Ryu, N. Khanarian, C. Tung, D. Tank, and R. H. Austin, *Nano Lett.* 6, 169 (2006).
3. K. Kuningas, T. Rantanen, T. Ukonaho, T. Lövgren, and T. Soukka, *Anal. Chem.* 77, 7348 (2005).
4. E. Downing, L. Hesselink, J. Ralston, and R. Macfarlane, *Science* 273, 1185 (1996).
5. P. A. Tick, N. F. Borrelli, L. K. Cornelius, and M. A. Newhouse, *J. Appl. Phys.* 11, 6367 (1995).
6. G. F. J. Garlick and C. L. Richards, *J. Lumin.* 9, 432 (1974).
7. X.-X. Luo and W.-H. Cao, *Sci. China. Ser. B. Chem.* 50, 505 (2007).
8. P. N. Yocom, J. P. Wittke, and I. Ladany, *Metall. Trans., A, Phys. Metall. Mater. Sci.* 2, 763 (1971).
9. L. Ozawa, *J. Electrochem. Soc.* 124, 413 (1977).
10. C. L. Lo, J. G. Duh, B. S. Chiou, C. C. Peng, and L. Ozawa, *Mat. Chem. Phys.* 71, 179 (2001).
11. P. C. Becker, N. A. Olsson, and J. R. Simpson, *Erbium Doped Fiber Amplifiers-Fundamentals and Technology*, Academic Press, New York (1999).
12. M. J. M. Diggonet (ed.), *Rare Earth Doped Fiber Lasers and Amplifiers*, Marcel Dekker Inc, NY (1993).
13. A. A. Kaminskii, *Laser Crystals, Their Physics and Properties*, Springer Verlag, Berlin (1981).
14. B. R. Judd, *Phys. Rev.* 127, 750 (1962).
15. G. S. Ofelt, *J. Chem. Phys.* 37, 511 (1962).
16. http://en.wikipedia.org/wiki/CIE_1931_color_space.
17. C. S. McCamy, *Color. Res. Appl.* 17, 142 (1992).