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Effect of crystallite size on electron spin resonance of Gd^{3+} and luminescence of Eu^{3+} doped in La_6WO_{12}

V Rama Devi[a], B Vijaya Kumar[a,b], Radha Velchuri[a], Palla Suresh[a], G Ravi[a] & M Vithal[a]*

[a]Department of Chemistry, Osmania University, Hyderabad 500 007, India

[b]Department of Chemistry, National Institute of Technology, Warangal 506 004, India

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Nano-sized Eu^{3+} and Gd^{3+} doped lanthanum tungstates of composition $La_{6-x}Ln_xWO_{12}$ (Ln = Eu, Gd; $0 \le x \le 0.2$) are prepared by sol-gel complexation method. These samples are characterized by powder X-ray diffraction (XRD). The average crystallite size is calculated from the XRD using Scherer's equation. The electron spin resonance (ESR) spectrum of Gd^{3+} doped lanthanum tungstate (La_6WO_{12}) gives characteristic "U" type spectrum. The luminescence spectrum of Eu^{3+} doped La_6WO_{12} gives characteristic $^5D_0 \rightarrow {}^7F_n$ (n = 0 to 4) bands due to trivalent europium ions. The intensity of $^5D_0 \rightarrow {}^7F_2$ transition decreases with increase in the sintering temperature due to depletion of surface Eu^{3+} ions. The intensity of $^5D_0 \rightarrow {}^7F_2$ sintered at 700°C has highest intensity and may have laser applications.

Keywords: Sol-gel, Powder XRD, Crystallite size, Luminescence, ESR

Materials with mixed conductivity (ionic and electronic) at high temperatures and chemically stable are of considerable interest in solid oxide fuel cells (SOFC) and hydrogen gas separation membranes. Oxides with high proton conductivity find potential applications in both hydrogen production and hydrogen separation. A survey of literature data on electrical properties shows that rare-earth tungstate of composition Ln_6WO_{12} (Ln = lanthanide) are promising materials for hydrogen permeable membranes due to their mixed conductivity and remarkable stability in moist CO_2 environments[1-3]. These lanthanide tungstate oxides, Ln_6WO_{12}, have a defect fluorite structure and they can be formulated as $Ln_6WO_{12}k_2$ or $A_4O_{6.85}\ k_{1.15}\ (k= \ddot{v})_O$ for a fluorite formulation. The type of lattice adopted by Ln_6WO_{12} oxides depends on the ionic radii of Ln^{3+}. The structure of Ln_6WO_{12} is characterized by seven edge-sharing cubes with oxygen ions in the corners. The tungsten ion is in the middle of central cube while the lanthanide ions are in the center of neighboring six cubes. The central cube has two oxygen vacancies located at opposite vertex positions. Each of these six rare earth containing cubes shares one of the vacant corners with central W-containing cube[4]. It is well known that the preparation method influences the properties, microstructure and size distribution of materials considerably. Wet chemical methods are found to be effective to obtain stoichiometric oxides at lower temperatures compared to conventional solid state method. Lower sintering temperatures are desirable for the synthesis of tungstates due to their volatile nature. Studies pertaining to preparation of nanosized Ln_6WO_{12} compositions and/or the influence of crystallite size on ESR and emission profiles, to our knowledge, are not reported. In this paper, we present the preparation of $La_{6-x}Ln_xWO_{12}$ (Ln = Gd, (x = 0.02, 0.05, 0.1, 0.2), Eu (x = 0.05)) and the effect of crystallite size on ESR of Gd^{3+} and emission of Eu^{3+} profiles.

Experimental Procedure

Rare earth oxides, Ln_2O_3 (Ln = La, Gd and Eu) (Indian rare earth Ltd, purity 99%), Tungsten powder (Aldrich 99.9%), H_2O_2 (SD-Fine 30%), citric acid, ammonia solution (SD-Fine, 25%), concentrated HNO_3 (SD-Fine) were used as starting materials as received.

Solution "A": Stoichiometric amounts of Ln_2O_3 dissolved in concentrated HNO_3 to form rare earth nitrate. Excess nitric acid was removed by slow heating. The resultant solid was dissolved in 25 mL of distilled water.

Solution "B": Calculated amount of tungsten powder was dissolved in 10 mL of H_2O_2.

Solution "A" was mixed with solution "B" with constant stirring. Then citric acid was added to this

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*Corresponding author (E-mail: mugavithal@gmail.com) solution, such that the mole ratio of citric acid to metal ion is 2:1. At this stage, metal citrates are believed to be formed. The pH of the resultant metal citrate solution was adjusted to 6-7 by adding dilute ammonia solution drop-wise. The solution was then slowly evaporated on a hot plate till a viscous liquid was obtained. At this stage ethylene glycol was added in the molar ratio, citric acid: ethylene glycol = 1:1.2. This mixture was heated on a hot plate at 100°C for 2-3 h with constant stirring. The temperature was increased to 160-180°C, at the onset of solidification. The ensuing porous solid mass was ground in an agate mortar using spectral grade. The resultant solid (named as “Precursor”) was divided into several parts. Each part was heated separately in muffle furnace at various temperatures (700-1000°C) for 5 h to obtain the desired rare earth tungstates, La_6WO_{12}, $La_{6-x}Gd_xWO_{12}$ (x = 0.02, 0.05, 0.1 and 0.2) and $La_{6-x}Eu_xWO_{12}$ (x = 0.05).

The powder X-ray diffractograms were recorded on Shimadzu XRD-7000 powder X-ray diffractometer using Ni filtered monochromatic Cu Kα radiation of wavelength 1.5418 Å. The scan rate is 2°/min in the range 2θ = 10-80°. The room temperature ESR spectra were recorded on a JOEL PE-3X, X-band spectrometer equipped with 100 kHz field modulation unit. The ESR spectrometer was optimized for modulation amplitude, receiver gain, time constant and scans time. Photoluminescence spectra were recorded with a Flourolog spectrophotometer equipped with a 40 W Xenon lamp as the excitation source of radiation at room temperature.

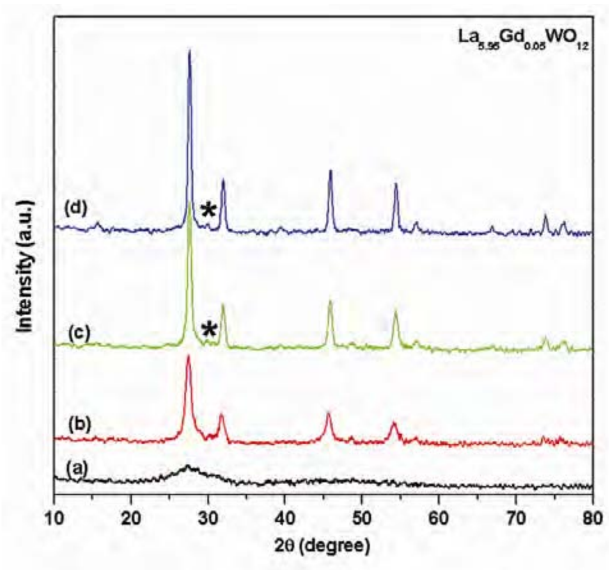

Fig.1—Powder XRD of $La_{5.95}Gd_{0.05}WO_{12}$ calcined at (a) 700°C, (b) 800°C, (c) 900°C and (d) 1000°C

Results and Discussion

Powder X-ray diffraction

The powder X-ray diffraction of all the samples heated up to 600°C did not give any diffraction lines indicating the absence of long range order. The diffraction lines were observed for $La_{5.95}Eu_{0.05}WO_{12}$ and $La_{6-x}Gd_xWO_{12}$ (x = 0.02, 0.05, 0.1 and 0.2) samples heated at 700 and 800°C respectively. The powder XRD of $La_{6-x}Ln_xWO_{12}$ (Ln = Gd and Eu) samples are similar to that reported for La_6WO_{12} [JCPDS Card No. 30-0686]. The powder XRD patterns of $La_{5.95}Gd_{0.05}WO_{12}$ and $La_{5.95}Eu_{0.05}WO_{12}$ are shown in Figs 1 and 2, respectively. The broad base line observed for $La_{5.95}Eu_{0.05}WO_{12}$ samples heated at 700 and 800°C indicate the presence of amorphous phase along with crystalline lanthanide tungstate phase. The relatively large line width observed for samples heated up to 1000°C indicate the nano nature of the samples. The crystallite size was estimated from the line width of intense line using Scherer’s equation and given in Table 1. In the case of $La_{5.95}Gd_{0.05}WO_{12}$ (sintered at 900 and 1000°C) and $La_{5.95}Eu_{0.05}WO_{12}$ (sintered at 900°C) samples, a diffraction peak of low intensity is observed at 2θ = 29.95°. It is identified as La_2O_3 (shown by * in Figs 1 and 2). The weight percentage of impurity peak obtained from the relative intensity ratio of (2 2 2) of La_6WO_{12} and (1 0 1) of La_2O_3 is found to be 8 wt% for $La_{5.95}Eu_{0.05}WO_{12}$ and 2 wt% for $La_{5.95}Gd_{0.05}WO_{12}$. The intensity of impurity (La_2O_3) peak decreased with

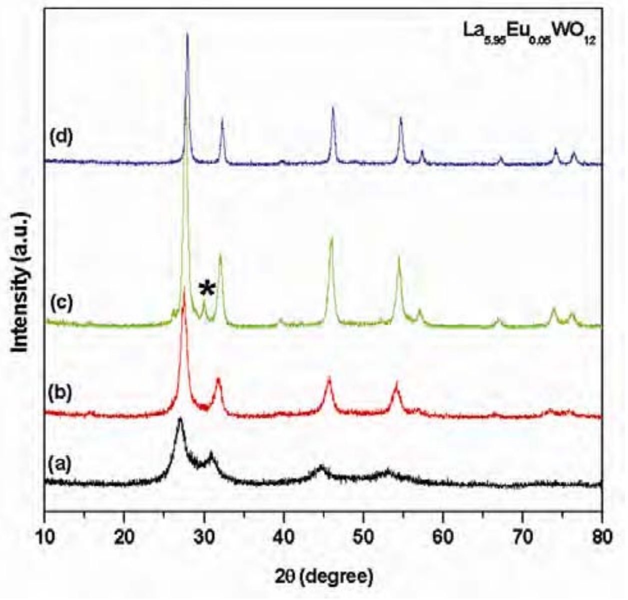

Fig. 2— Powder XRD of $La_{5.95}Eu_{0.05}WO_{12}$ calcined at (a) 700°C, (b) 800°C, (c) 900°C and (d) 1000°C

Table 1– Crystallite size of $La_{5.95}Gd_{0.05}WO_{12}$ and $La_{5.95}Eu_{0.05}WO_{12}$ samples sintered at different temperatures

Compound	Temperature (°C)/5 h	Crystallite size (nm)
$La_{5.95}Gd_{0.05}WO_{12}$	700	-
	800	10
	900	17
	1000	20
$La_{5.95}Eu_{0.05}WO_{12}$	700	5
	800	9
	900	13
	1000	18

increase in the sintering temperature in all the samples. It is reported that La_6WO_{12} ($A_6A^1O_{12}$) compounds crystallize in face centered cubic lattice and can be classed as disordered pyrochlore with a = 11.18 Å[5]. The XRD patterns of $La_{5.95}Eu_{0.05}WO_{12}$ and $La_{5.95}Gd_{0.05}WO_{12}$ samples heated at 1000°C were least square fitted using the POWD software[6] to obtain unit cell parameters. The observed 2θ values and unit cell parameters of La_6WO_{12} were given as input parameters to obtain the unit cell parameters and calculated *d*-lines for $La_{5.95}Eu_{0.05}WO_{12}$ and $La_{5.95}Gd_{0.05}WO_{12}$. The unit cell parameter (*a* in Å) for $La_{5.95}Gd_{0.05}WO_{12}$ and $La_{5.95}Eu_{0.05}WO_{12}$ was found to be 11.18 X± 0.005 and 11.25X ± 0.005 Å, respectively. Thus, both $La_{5.95}Gd_{0.05}WO_{12}$ and $La_{5.95}Eu_{0.05}WO_{12}$ crystallized in disordered pyrochlore lattice.

As mentioned, the XRD patterns of $La_{5.95}Gd_{0.05}WO_{12}$ and $La_{5.95}Eu_{0.05}WO_{12}$ were characterized by the presence of La_2O_3 impurity along with disordered pyrochlore phase. Chang and Phillips[5] have reported that the reaction between La_2O_3 and WO_3 to form La_6WO_{12} was completed at 1400°C after 6 h of heating. Yoshimura and Rouanet[7] have shown that La_6WO_{12} (La/W = 6) is a high temperature phase that decomposes to $La_{10}W_2O_{21}$ (La/W = 5) and La_2O_3 at temperatures below 1740°C. Both La_6WO_{12} and $La_{10}W_2O_{21}$ (La/W = 5) have similar XRD patterns which probably means that they have same structure as well. Magraso *et al.*[8] in their detailed investigation, have reported that segregations of either La_2O_3 or $La_6W_2O_{15}$ were found when La/W $\geq$ 5.8 and $\leq$ 5.2, respectively. Thus, the presence of La_2O_3 impurity in the present investigation is in accordance with earlier reports in the La-W-O system in view of the existence of La/W ratios ranging from 6 to 5[8]. It is observed that Eu_6WO_{12} and Gd_6WO_{12} crystallize in cubic and tetragonal lattice respectively[9]. Both La_6WO_{12} and Eu_6WO_{12} crystallize in cubic lattice and hence Eu^{3+} occupies La^{3+} position in the La_6WO_{12} lattice. When Gd^{3+} is doped into La_6WO_{12} lattice, the guest ion may or may not occupy the La site as both end members have different crystal structures. But the powder X-ray diffractograms of both $La_{5.95}Gd_{0.05}WO_{12}$ and La_6WO_{12} are similar to each other and therefore Gd^{3+} is believed to occupy La^{3+} position in the La_6WO_{12} lattice.

Electron spin resonance of $La_{6-x}Gd_xWO_{12}$ (x = 0.02, 0.05, 0.1 and 0.2)

The ground state of Gd^{3+} with $4f^7$configuration is $^8S_{7/2}$. For such an ion (L = 0), the Hamiltonian consists of Zeeman and crystal field terms. When the crystal field is negligible (absence of single-ion anisotropy), the Hamiltonian is composed of only Zeeman term and in the presence of applied magnetic field gives a single broad line centered at g = 2.0. However, strong spin-orbit coupling of 4f electrons breaks the L-S scheme and the ground state ($^8S_{7/2}$) is mixed with L $\neq$ 0 states giving rise to a crystal field which is comparable to exchange coupling energy. Due to this mixing of states, the ESR spectrum of both single crystal and powders of Gd^{3+} is characterized by several lines depending on the local symmetry of Gd^{3+} ion[10].

La_6WO_{12} gave no ESR signal while $La_{6-x}Gd_xWO_{12}$ (x = 0.02, 0.05, 0.1 and 0.2) gave clear ESR signals at room temperature. It is noticed that the ESR spectra of $La_{6-x}Gd_xWO_{12}$ (x = 0.02, 0.05 and 0.1) were characterized by several lines with different g values while for $La_{5.8}Gd_{0.2}WO_{12}$ (x = 0.2) single broad resonance was observed. The ESR spectra of $La_{6-x}Gd_xWO_{12}$ (x = 0.02 to 0.1) were characterized by peaks with effective g-values at ~6.0 – 6.2, 2.7 – 2.8 and 2.0 – 2.05 which are known to constitute the “U” spectrum[11]. The critical concentration for the observation of “U” spectrum seems to be for compositions with $x \leq 0.1$. The intensity of “U” spectral features increases from x = 0.02 to 0.05 and remains almost constant up to x = 0.1. The present discussion is with reference to $La_{5.95}Gd_{0.05}WO_{12}$ sample. Figure 3 shows the room temperature ESR spectra of $La_{5.95}Gd_{0.05}WO_{12}$ prepared at different temperatures (700-1000°C). The “U” spectral features are observed for $La_{5.95}Gd_{0.05}WO_{12}$ samples sintered at 700°C (amorphous) and above 700°C (crystalline). Each spectrum consists of five peaks at g ~ 6.0 - 6.2, 4.2 - 4.4, 2.7 - 2.8, 2.2 - 2.3 and 2.0 - 2.05. These

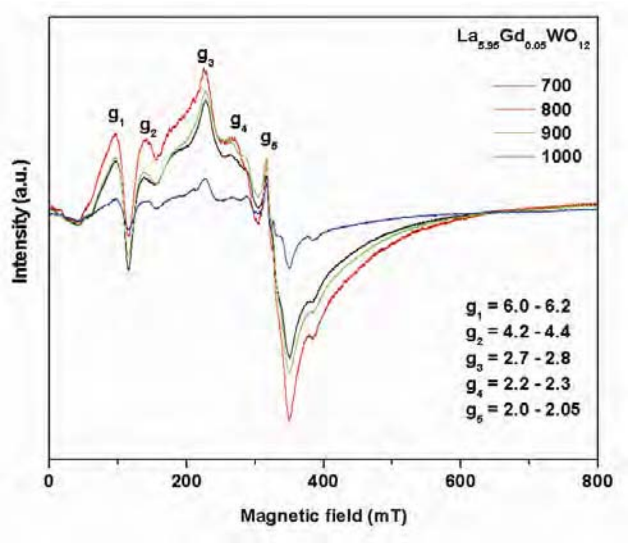

Fig. 3—Powder ESR spectra of $La_{5.95}Gd_{0.05}WO_{12}$ calcined at 700°C, 800°C, 900°C and 1000°C

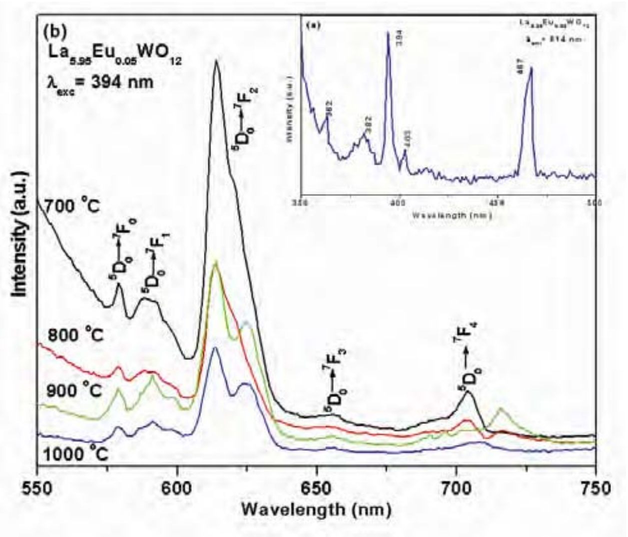

Fig. 4—(a) Excitation (inset) and (b) emission spectra of $La_{5.95}Eu_{0.05}WO_{12}$

spectra are similar to those reported for Gd: Na-Y Zeolite crystals[11], Gd: SiO2-Na_2O[12], Gd: ZnO-P_2O_5[13] and $La_{1.95}Gd_{0.05}Zr_2O_7$[14]. It is well known that the "U" spectra for Gd^{3+} are observed when the rare earth ion is in a glassy matrix or in disordered lattice[15]. In the present investigation, La_6WO_{12}, $La_{5.95}Gd_{0.05}WO_{12}$ and $La_{5.95}Eu_{0.05}WO_{12}$ are crystallized in disordered pyrochlore lattice and hence, "U" spectral features are observed for $La_{5.95}Gd_{0.05}WO_{12}$ samples.

The variation in intensity of the electron spin resonance spectrum with sintering temperature of $La_{5.95}Gd_{0.05}WO_{12}$ follows the order 800 > 900 > 700 > 1000°C. At 700°C, $La_{5.95}Gd_{0.05}WO_{12}$ was found to be amorphous which was confirmed by its powder XRD. At 800°C, the sample was found to be crystalline and the number of Gd^{3+} ions increases on the surface. Hence, the highest intensity is observed at this temperature. Above this temperature, the number of Gd^{3+} ions decreases on the surface due to the increase in the crystallite size resulting a decrease in the intensity.

Luminescence of $La_{5.95}Eu_{0.05}WO_{12}$

Figure 4a (inset) shows the excitation spectrum of $La_{5.95}Eu_{0.05}WO_{12}$ monitoring the emission at 614 nm. The excitation bands observed at 362, 382, 394 and 403 nm are identified as $^7F_0\rightarrow{}^5D_4$, $^7F_0\rightarrow{}^5L_7$, $^7F_0\rightarrow{}^5L_6$ and $^7F_0\rightarrow{}^5D_3$ respectively. The intense peak observed at 394 nm has been selected as excitation wavelength for the measurement of emission spectra of $La_{5.95}Eu_{0.05}WO_{12}$. Figure 4b shows the emission spectra of $La_{5.95}Eu_{0.05}WO_{12}$ calcined at 700, 800, 900 and 1000°C. The emission bands observed at about 579, 592, 614, 656 and 704 nm are assigned to the transitions from the $^5D_0$ level to the $^7F_0$, $^7F_1$, $^7F_2$, $^7F_3$, and $^7F_4$ levels respectively[16]. The intensity of $^5D_0\rightarrow{}^7F_2$ transition is found to depend on the calcination temperature. The variation in intensity of this transition follows the order 700 > 800 > 900 > 1000°C. The crystallite size increases with increase in the calcination temperature due to the growth of individual grains and/or oriented coalescence of the primary small grains. At 700°C, the number of Eu^{3+} ions on the surface is more and hence emission intensity for all the transitions was found to be highest. As the calcination temperature increases, the particles size increases leading to a decrease in the number of Eu^{3+} ions on the surface. Therefore, the emission intensity decreases with increase in the sintering temperature. Thus $La_{5.95}Eu_{0.05}WO_{12}$ sintered at 700°C has possible application as laser material. It is well known that the probability of the electric dipole $^5D_0\rightarrow{}^7F_2$ transition is very sensitive to the changes in the chemical surroundings of the Eu^{3+} ions. On the other hand, $^5D_0\rightarrow{}^7F_1$ emission at 592 nm is a magnetic-dipole transition which is independent of rare earth ion surroundings. When Eu^{3+} ions are situated at low-symmetry sites, the electric-dipole transition has larger probability than the magnetic-dipole transition[17,18]. In the present investigation, the electric-dipole transition has more probability than the magnetic-dipole transition due to the low symmetry of the Eu^{3+} ions in the host lattice La_6WO_{12}. These results are consistent with powder XRD results.

Conclusions

Rare earth doped lanthanum tungsten oxides of composition $La_{6-x}Ln_xWO_{12}$ (Ln = Gd (x = 0.02, 0.05, 0.1 and 0.2) and Eu (x = 0.05)) were prepared by sol-gel process. All the compositions were characterized by powder XRD and crystallized in disordered pyrochlore lattice. The "U" type ESR spectrum was observed for all $La_{6-x}Gd_xWO_{12}$ compositions with $x \leq 0.1$. The ESR spectrum of $La_{5.95}Gd_{0.05}WO_{12}$ shows maximum intensity for the sample calcined at 800°C. The variation in intensity of "U" spectrum with sintering temperature was explained on the basis of number of surface Gd^{3+} ions. The emission spectra of $La_{5.95}Eu_{0.05}WO_{12}$ gave characteristic peaks corresponding to transitions from $^5D_0$ to ^7F_n (n = 0 to 4). The electric dipole ($^5D_0 \rightarrow ^7F_2$) transition has more intensity than the magnetic dipole ($^5D_0 \rightarrow ^7F_1$) transition indicating Eu^{3+} ions are situated at low symmetry sites in the host lattice of La_6WO_{12}.

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