Optical and magnetic properties of (Er, F) co-doped SnO₂ nanocrystals

Vinod KUMAR, Sitharaman UMA, Rajamani NAGARAJAN*
Materials Chemistry Group, Department of Chemistry, University of Delhi, Delhi, India

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Abstract: Uniformly (Er, F) co-doped SnO₂ nanocrystals, obtained by a low-temperature solution-based method, were characterized by a variety of analytical techniques. The structure, morphology, and ratio of the elements were confirmed by PXRD, SEM, and TEM analysis, respectively. From XPS analysis, atomic concentrations of Sn, O, and F were quantified. Interparticle pore size increased significantly (with a mean pore diameter of 25.82 nm) in the co-doped sample. Higher in-plane oxygen vacancies and bands due to multiphonon scattering were observed in the Raman spectrum of the sample. The defect traps in the sample were experimentally determined using TL spectroscopy. A broad intense glow curve at 485 K and a weak emission at 600 K in the TL spectrum were quenched on exposure to UV radiation. A large blue shift of the exciton absorption (due to the Moss–Burstein effect) and sharp bands due to intraconfigurational f–f transitions were observed for (Er, F) co-doped SnO₂ with an estimated band gap of 4.18 eV. From the photoluminescence spectral studies, 3 types of emission centers at 471 nm, 546 nm, and 627 nm were detected. Co-doping stabilized ferromagnetism in SnO₂ at room temperature.

Key words: Luminescence, ferromagnetism, defects, Moss–Burstein effect, nanocrystalline

1. Introduction
Various chemical strategies such as cation doping, anion doping, cation–cation co-doping, cation–anion co-doping, and anion–anion co-doping are being adopted to engineer the band gap of wide band gap oxide semiconductors, ZnO, TiO₂, CeO₂ and SnO₂ [1–5]. Among these, the cation–anion co-doping strategy is the least investigated and is gaining momentum for the following reasons: 1) it introduces charge compensation between dopants, thereby reducing the number of recombination centers and promoting the electron–hole pair separation to stimulate the change in the band gap by eliminating the impurity states; 2) it can facilitate the overall mixing of the impurity states and VB/CB by adjusting the position of the band gap to obtain an optimized narrow value; 3) it can effectively reduce the formation energy of the combination defects as compared to singly doped systems. Among the co-dopants, doping with 2 cations has been pursued due to the easy experimental conditions for their fabrication [6,7]. Anion–anion co-doping of these oxides is increasingly becoming viable by solution-based synthetic methods [8,9]. The cation–anion co-doping approach produces changes in the conduction and valence bands of these semiconductors simultaneously and can manifest in many interesting optoelectronic properties arising from the defect chemistry and physics, leading to expansion of functions.

SnO₂, an n-type wide band gap semiconductor, enjoys a unique status for exhibiting multifunctions for a variety of reasons such as larger exciton binding energy and high chemical and mechanical stabilities...

*Correspondence: rnagarajan@chemistry.du.ac.in
with unique photoelectronic properties [1,10]. The multifunctional character of SnO$_2$ basically emerges from the flexible nature of the structure, having cations with mixed valence states and anions with deficiencies (vacancies). The greater contributions of lattice vibrations in imparting applications to SnO$_2$ for its use as solid-state gas sensor material, oxidation catalyst, and transparent conductor have been excellently reviewed in the literature [11]. As compared to single cation or anion doping in SnO$_2$, studies on cation-anion co-doped systems are few. Nb/F co-doped SnO$_2$ thin films were fabricated by spray pyrolysis procedure by Turgut et al. [12] with the primary objective of tuning the optoelectronic properties, in which the niobium content was varied between 0 and 4 at.% with fixed fluoride content of 10 wt.%. Huang et al. [13] synthesized gallium and nitrogen co-doped tin oxide (SnO$_2$: Ga/N) films at 500 °C using the MOCVD method to tune the band gap and the conductivity. Moharrami et al. [14] investigated the co-doping of S and Al in SnO$_2$ films deposited by spray pyrolysis technique. The optical band gap values were found to be in the range of 3.8–4.2 eV. Majority charge carriers were found to change from electrons to holes for S-doping in SnO$_2$: Al (40 at.%) thin films. On increasing sulfide concentration, impurity phases such as S, SnS, SnS$_2$, and Sn$_2$S$_3$ were observed along with cassiterite SnO$_2$. The best photoconductive property was realized for SnO$_2$ thin films co-doped with 40 at.% Al and 5 at.% S. Fe-N co-doped SnO$_2$ powders were synthesized by chemical coprecipitation method and their magnetization studies were reported [15]. The hole (defect) generated by the nitrogen doping at the oxygen site induced ferromagnetism in the SnO$_2$ samples, quite the opposite of the singly Fe-doped SnO$_2$ exhibiting a paramagnetic character.

Rare earth ions having rich spectroscopic properties have been the prime choice for cations so as to append spectroscopic functions to SnO$_2$. Furthermore, Er-doped SnO$_2$ structures have been reported as potential candidates as waveguides, electroluminescent displays, or building blocks for advanced materials [16]. While numerous reports are available on the F-doping of SnO$_2$ (both in films and in powders) [17,18], limited studies exist on Er-doping in SnO$_2$ because of the enormous size difference between Er$^{3+}$ and Sn$^{4+}$ and the preference of Er$^{3+}$ to have coordination numbers greater than 6 [16,19–21]. The present paper describes the synthesis of SnO$_2$ nanocrystals co-doped with Er$^{3+}$ and F$^{-}$ using a single-source precursor. The obtained nanocrystals were characterized by powder X-ray diffraction (PXRD) patterns and SEM, TEM, XPS, UV-visible diffuse reflectance spectroscopic, Raman spectroscopic, and photoluminescence (PL) spectroscopic techniques. Surface area and pore size analyses of the co-doped SnO$_2$ samples were performed. Various trapped states were analyzed by thermoluminescence (TL), a powerful spectroscopy technique that determines the localized states as well as the recombination centers leading to radiative transition simultaneously. As the co-doping approach has been found to induce ferromagnetic ordering in wide band gap semiconductors such as ZnO, TiO$_2$, and SnO$_2$ [22,23], the magnetic interactions between the hole and the electrons in the (Er, F) co-doped SnO$_2$ system was also studied.

2. Experimental

2.1. Synthesis

Er and F co-doped SnO$_2$ nanocrystals were prepared using a single-source precursor approach [17]. First, 1 mol% Er-doped KSnF$_3$ was synthesized from SnCl$_2.2$H$_2$O (99.9%, Sigma Aldrich), KF (99%, AR grade, CDH), and ErCl$_3.6$H$_2$O (99.9%, Sigma Aldrich). Typically, 1.128 g of SnCl$_2.2$H$_2$O, 0.0065 g of ErCl$_3.6$H$_2$O, and 0.8715 g of KF were mixed in methanol and kept for 2 h under constant stirring. A white-colored suspension appeared and it was separated by centrifugation and washed several times with distilled water. Next, 0.25 g of
1 mol% Er-doped KSnF$_3$ was refluxed with a mixture containing 30 mL of 30% H$_2$O$_2$ and 70 mL of methanol (CH$_3$OH) for 10 h at 100 °C. A white-colored suspension was obtained, was separated by centrifugation, and was dried naturally over a desiccant.

2.2. Characterization

PXRD patterns were recorded using a high-resolution PANanalytical diffractometer, equipped with PIXcel$^{3D}$ detector employing CuK$_\alpha$ radiation ($\lambda = 1.5418$ Å) with a scan rate of 1.0 s/step and a step size of 0.02° at 298 K over the range of 2θ = 15°–70°. Diffuse reflectance spectra of the samples were obtained using a PerkinElmer UV-Vis spectrophotometer Lambda-35 with BaSO$_4$ as the reference. Thermogravimetric analysis was carried out using a PerkinElmer Pyris Diamond in nitrogen atmosphere at the heating rate of 5 °C/min from 25 to 900 °C. FT-IR spectra were collected using a PerkinElmer 2000 spectrometer using KBr disks. Raman spectra were recorded using a Renishaw system with an Ar$^+$ laser ($\lambda = 514.5$ nm). The Brunauer–Emmett–Teller (BET) surface area of the samples was obtained from physical adsorption of N$_2$ at 77 K using a Belsorp-Max and Belsorp-Aqua Porosimeter. Magnetic measurements were carried out at 300 K using a vibrating sample magnetometer (Microsense EV9). TEM images were recorded on a Philips Tecnai G$^2$ 30 transmission electron microscope with 300 kV accelerating voltage. SEM and EDX analysis was performed using a Hitachi S-3700 M microscope. PL measurements were carried out using Horiba Jobin Yvon equipment employing a CW xenon lamp source at room temperature. TL glow curves of the compacted (Er, F) co-doped SnO$_2$ samples were recorded using a Harshaw HT Reader 3500 at a heating rate of 3 K/s. Kinetic parameters were determined by the glow curve deconvolution method as implemented in the Glow Fit V1.1 program developed and distributed by Puchalska and Bilski [24]. XPS measurements were carried out using a Thermo K$_\alpha$ XPS instrument at a pressure of better than 10$^{-9}$ Torr. The core-level spectra were collected using MgK$_\alpha$ radiation (photon energy = 1253.6 eV) at a pass energy of 50 eV, an electron take-off angle of 90°, and a resolution of 0.1 eV.

3. Results and discussion

The PXRD pattern of 1 mol% Er-doped KSnF$_3$ (Figures 1a and 1b) obtained by a simple and green precipitation procedure is shown in Figure 1a, and it showed triclinic symmetry as reported in JCPDS file no. 81-1104. No other crystalline impurity was observed in the pattern. The PXRD pattern of the oxidation product of Er-doped KSnF$_3$ with H$_2$O$_2$ suggested the formation of rutile-structured SnO$_2$ (JCPDS file no. 41-1445) (Figure 1a). The average crystallite size estimated from the Scherrer analysis is ~3 nm. The elemental mapping by EDX analysis of the SEM image of this sample is shown in the inset of Figure 1a, indicating the presence of Er and F in addition to Sn and O in the samples. For the purpose of comparison, 1 mol% Er-doped SnO$_2$ was synthesized by reacting a mixture of SnCl$_2$·2H$_2$O and ErCl$_3$ with H$_2$O$_2$ in methanol. Its PXRD pattern is presented in Figure 1a.

To quantify the elements in the co-doped SnO$_2$ sample, high-resolution core-level XPS spectral analysis was performed and is reproduced in Figure 2. The binding energies were calibrated using the C 1s hydrocarbon peak at 284.6 eV to compensate for surface charging effects. Peaks observed at 487.09 eV, 531.43 eV, and 684.94 eV were assigned to Sn 3d$_{5/2}$, O 1s, and F 1s, respectively, based on earlier reports [17,25]. Deconvolution of the F 1s peak suggested the presence of 2 different types of fluoride, i.e., surface and substituted. The peak present at a lower binding energy (684.47 eV) was attributed to the fluoride on the surfaces and the other peak present at a higher binding energy (685.78 eV) was assigned to fluoride ions substituted in the lattice [26]. Furthermore,
the Gaussian fit of Sn $3d_{5/2}$ showed the peaks positioned at 486.98 eV and 488.07 eV arising primarily from Sn$^{4+}$ species. No contribution from elemental Sn$^0$ atoms and Sn$^{2+}$ ions was noticed, usually known to occur at a binding energy of 485–486 eV \cite{27}. The O1$s$ peak, on deconvolution, gave 2 different types of oxygen. The peak at around 531.39 eV was assigned to O-Sn$^{4+}$ bonding and the peak at 531.87 eV was attributed to the nonstoichiometric oxides present in the surface region \cite{28,29}. The atomic concentrations of Sn, O, and F were 23\%, 44\%, and 33\%. The peak due to Er was not noticed in XPS due to its very low concentration, thus limiting its detection beyond a specific depth.

Figure 1. a) PXRD pattern of 1 mol\% Er-doped KSnF$_3$ (black line) and oxidized product from 1 mol\% Er-doped KSnF$_3$ (blue line). Inset shows SEM image and EDX analysis of the oxidized product from 1 mol\% Er-doped KSnF$_3$. b) PXRD pattern of 1 mol\% Er-doped SnO$_2$. Inset shows Williamson–Hall plot of Er-doped SnO$_2$.

Generally, a major contribution to the broadening of the Bragg reflections was obtained from the strain present in the crystallites as well as their reduced size. The strain in the co-doped sample was calculated following the Williamson and Hall theorem \cite{30}:

$$\beta \cos \frac{\theta}{\lambda} = \frac{1}{D} + \eta \sin \frac{\theta}{\lambda}$$

where $\beta$ is the full width at half-maximum in radian, $\theta$ is the diffraction angle, $\lambda$ is the X-ray wavelength, $D$ is the effective particle size, and $\eta$ is the effective strain. The strain and the crystallite size ($D$) were measured from the slope and from the intercept of linear fit of $\beta \cos \theta / \lambda$ versus $\sin \theta / \lambda$, respectively. A positive slope of +0.020 indicated the tensile strain across (Er, F) co-doped SnO$_2$ nanocrystals arising from the reduced size of the crystallites (Figure 3) \cite{31}. Since the doped fluoride ion concentration was quite high (with the simultaneous presence of lower valent Er$^{3+}$), to maintain charge balance, increase in density of oxygen vacancies (OVs) might occur. As a result, the effective columbic repulsion between the tin ions would also increase, contributing to the strain of these crystals. The Williamson and Hall plot of Er-doped SnO$_2$ (shown in the inset of Figure 1b) suggested a positive compressive strain in the samples, making clear that co-doping was indeed responsible for the tensile strain in these samples. Though these results gave only qualitative information, the effect of them can be realized from the peak shapes in Raman and PL spectra, as discussed later. The calculated crystallite size from the intercept was $\sim$4 nm for (Er, F) co-doped SnO$_2$ nanocrystals, matching well with the average crystallite size estimated using Scherrer analysis.
Figure 2. XPS core level spectra of (Er, F) co-doped SnO$_2$ of Sn 3$d_{5/2}$, O 2$p$, and F 1$s$.

Figure 3. Williamson-Hall plot of (Er, F) co-doped SnO$_2$. Inset shows TEM image of (Er, F) co-doped SnO$_2$.

Agglomeration of particles, due to high surface forces such as van der Waals and capillary forces, was observed in the TEM images (shown in the inset of Figure 3). The crystallite size, from TEM images, was in agreement with the Scherrer analysis. A porous morphology was revealed in the SEM micrographs of (Er, F) co-doped SnO$_2$ (inset of Figure 1a), which was further confirmed from BET analysis. N$_2$ adsorption–desorption
isotherms of (Er, F) co-doped SnO$_2$ and Er-doped SnO$_2$ (Figure 4a). The corresponding pore properties, including BET surface area, pore volumes, and pore sizes, are summarized in Table 1. Mean pore diameter increased from 2.62 nm (Er-doped SnO$_2$) to 25.82 nm ((Er, F) co-doped SnO$_2$) and indicated change in the porosity of the sample arising primarily from the heavy anion (F$^-$) doping of the system. Although such values were reported earlier [32,33], the observed mesopore size was higher than in the singly doped SnO$_2$ systems. (Er, F) co-doped SnO$_2$ at room temperature exhibited characteristic curve-type IV isotherms with distinct capillary condensation steps, suggesting uniform mesopores [32,33]. Thermogravimetric traces of (Er, F) co-doped and Er-doped SnO$_2$ samples in flowing nitrogen atmosphere are presented in Figure 4b. While (Er, F) co-doped SnO$_2$ showed a slow and gradual weight loss up to 17% in the temperature range of 50–900 °C, drastic weight loss was observed for the Er-doped SnO$_2$. From the gradual weight loss behavior, it was clear that the dopants in SnO$_2$ were homogeneously distributed and were thermally stable in the temperature range investigated.

Table 1. BET surface area, mean pore diameter, and total pore volume of (Er, F) co-doped SnO$_2$ and Er-doped SnO$_2$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>BET surface area (m$^2$/g)</th>
<th>Mean pore diameter (nm)</th>
<th>Total pore volume (cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Er, F) co-doped SnO$_2$</td>
<td>23.42</td>
<td>25.82</td>
<td>0.1009</td>
</tr>
<tr>
<td>Er-doped SnO$_2$</td>
<td>175.21</td>
<td>2.62</td>
<td>0.1002</td>
</tr>
</tbody>
</table>

The FT-IR spectrum of (Er, F) co-doped SnO$_2$ nanocrystals is shown in the inset of Figure 5a, in which bands at 562 cm$^{-1}$ and 640 cm$^{-1}$ corresponding to the Sn-O vibrations can be located. The weakened intensity of the vibrational band at 640 cm$^{-1}$ was attributed to the inclusion of higher amounts of fluoride in the SnO$_2$ lattice [17]. The blue shift of the band centered at 562 cm$^{-1}$ (for the co-doped sample) from 553 cm$^{-1}$ (for the heavily F-doped SnO$_2$ sample) suggested the presence of higher concentration of OVs in them. The Raman spectrum of the (Er, F) co-doped SnO$_2$ nanocrystals is shown in Figure 5a. For comparison, the Raman spectrum of Er-doped SnO$_2$ is also presented in Figure 5a. Vibrational modes at 510, 588, 985, 1065, 1220, and 1353 cm$^{-1}$ were observed for the (Er, F) co-doped SnO$_2$, while the Er-doped SnO$_2$ showed bands at 323, 446, 570, 624, and 771 cm$^{-1}$. The band centered at 588 cm$^{-1}$ for (Er, F) co-doped SnO$_2$ nanocrystals was broad and intense, arising probably from the presence of higher concentrations of in-plane OVs and the inhomogeneous
strain present in the nanocrystals [34,35]. This peak was deconvoluted into 4 peaks centered at 588 cm$^{-1}$ (R1), 554 cm$^{-1}$ (R2), 462 cm$^{-1}$ (R3), and 635 cm$^{-1}$ (R4) as shown in Figure 5b. Peaks R1 and R2 were related to surface defects and R3 and R4 are fundamental modes $E_g$ and $A_{1g}$ (the bending mode of Sn-O-Sn) of SnO$_2$, respectively [36]. The band at 446 cm$^{-1}$ for Er-doped SnO$_2$ and at 462 cm$^{-1}$ for (Er, F) co-doped SnO$_2$ nanocrystals might arise from deeper OVs [37]. The interaction of Er$^{3+}$/F$^-$ ions in the SnO$_2$ lattice created changes in the vibrational modes, which are reflected in the disappeared and/or reduced Raman intensity [38]. Relaxation of the $k=0$ selection rule occurs in nanocrystals when the rate of disorder increases or the size decreases, and the infrared modes become weakly active when the structural changes induced by disorder and size effects take place [39]. For nanocrystals of SnO$_2$ (less than 16 nm in size), contributions from multiphonon processes are also observed in the high-frequency zone of the Raman spectrum [40]. The bands observed at 985, 1065, 1220, and 1353 cm$^{-1}$ in Figure 5a might possibly arise from the multiphonon scattering corresponding to $(E_g+E_g)$, $(E_g+A_{1g})$, $(A_{1g}+A_{1g})$, and $(A_{1g}+B_{2g})$ combinations, respectively. Earlier, such observations were reported for specific morphologies of pure SnO$_2$ (such as nanowires and nanobelts) [41,42]. Such multiphonon scattering was not present in Er-doped SnO$_2$ samples (Figure 5a). The presence of multiphonon scattering suggested the existence of deeper and shallow traps in (Er, F) co-doped SnO$_2$, which were experimentally detected employing TL spectroscopy measurements.

![Figure 5](image_url)

**Figure 5.** a) Raman spectrum of (Er, F) co-doped SnO$_2$ (blue line) and Er-doped SnO$_2$ (red line). Inset shows FT-IR spectrum of (Er, F) co-doped SnO$_2$ (blue circle) and Er-doped SnO$_2$ (red square). b) Deconvoluted Raman spectrum of (Er, F) co-doped SnO$_2$.

Diffuse reflectance spectra are shown in Figures 6a–6c. A large blue shift of the exciton absorption was observed in the UV-Vis diffuse reflectance spectrum of (Er, F) co-doped SnO$_2$ (Figure 6a) and the estimated band gap by the Kubelka–Munk function analysis was 4.18 eV (Figure 6c). The shift could be due to the combined effect of quantum size and the Moss–Burstein effects [43,44]. Additional experiments on the variation of absorption edge with temperature can provide crucial information on thermal activation threshold of this co-doped system as its shape is greatly influenced by the carrier–phonon interaction and the carrier–impurity interactions with increasing temperature. The UV-Vis diffuse reflectance spectrum of Er-doped SnO$_2$ is presented in Figure 6b. The inclusion of Er$^{3+}$ in SnO$_2$ was confirmed from the presence of sharp bands.
arising from intraconfigurational $f - f$ transitions from the $^4I_{15/2}$ ground state to the $^4I_{11/2}$, $^4I_{9/2}$, $^4F_{9/2}$, $^2H_{11/2}$, $^4F_{7/2}$, and $^4F_{5/2}$ excited states [16] (shown in the inset of Figure 6b). In addition to the $f - f$ transitions, a red shift of the band gap with respect to (Er, F) co-doped SnO$_2$ sample was noticed (Figure 6c). The red shift might be from fewer OVs in singly Er$^{3+}$-doped SnO$_2$ as compared to (Er, F) co-doped SnO$_2$.

The PL spectrum of (Er, F) co-doped SnO$_2$ in comparison to the Er-doped SnO$_2$ sample at room temperature is shown in Figure 7a. Increased intensity of the PL emission from (Er, F) co-doped SnO$_2$ samples was quite evident. The broad PL emission centered at 540 nm might be from defect electronic states as a result of co-doping as well as due to the inhomogeneous strain present in these nanocrystals. Such defect states might also be possible by b'bridging' OVs. In such a situation, electron excitation to the bulk shallow energy levels followed by return to the intragap level of SnO$_2$ corresponding to oxygen surface vacancies via radiative transitions might occur [45]. Presence of shoulder bands at 596 nm and 645 nm indicated strong orange and red emission, respectively. This strong orange luminescence was related to the bridging and in-plane OVs, which
form a series of metastable energy levels within the band gap [46]. The presence of broad luminescence bands in the range of 350–750 nm for the co-doped SnO$_2$ sample at room temperature suggested the existence of shallow trapped states within the band gap consisting of several subbands [47]. Upon deconvolution, 3 subbands at 471 nm, 546 nm, and 627 nm (Figure 7b) were evident, indicating the presence of 3 types of emission centers. The nature of the transition causing these emissions was generally thought to be Sn or O vacancies formed during the doping process, inducing deeper trapping states within the band gap. The band at 471 nm may originate from a shallower energy level located in the band gap compared to that of the 546 nm luminescence, as reported earlier [48]. The green emission at 546 nm and red emission at 627 nm could be from the $f - f$ transitions, $^4S_{3/2} \rightarrow ^4I_{15/2}$ and $^4F_{9/2} \rightarrow ^4I_{15/2}$, of Er$^{3+}$ ions, respectively. From the Raman and PL spectroscopy results, it was clear that the (Er, F) co-doped SnO$_2$ system was highly disordered in nature, consisting of many OVs.

**Figure 7.** a) PL emission spectra of (Er, F) co-doped SnO$_2$ (blue circle) and Er-doped SnO$_2$ (red square). b) Deconvoluted PL spectrum of (Er, F) co-doped SnO$_2$.

Without external irradiation, the (Er, F) co-doped SnO$_2$ nanocrystals showed a broad intense glow curve at 485 K and a weak emission at 600 K in the TL spectrum, signifying the presence of trapped states and shallow deeper traps, respectively (Figure 8a). It is noteworthy that no glow peak was observed for the Er-doped SnO$_2$ in the temperature range of 350–650 K (Figure 8a). Additionally, the glow curve in the (Er, F) co-doped SnO$_2$ occurred at a slightly higher temperature as compared to the heavily F-doped SnO$_2$ system (448 K) [18]. The OVs, due to the heavy doping of O$^{2-}$ ions with the F$^{-}$ ions, and the hole created by the co-dopant Er$^{3+}$ might possibly interact, leading to the formation of an appreciable concentration of trapped states resulting in intense TL emission [49]. In addition to this simple correlation, the (Er, F) co-doping might be creating deeper traps and increasing the density of the existing traps in addition to enhancing TL intensity. The creation of more OVs due to the introduction of F$^{-}$ and Er$^{3+}$ in the lattice suggested the possibility of creation of F and F$^{+}$ centers in the system. The trapped emission also demonstrated the correlation between the emission energy of the surface states and the quantum size effects in this system. The size effects on the surface states in the TL glow curves were discussed in detail in previous reports [50]. There are indications that OVs might be serving as traps for free electrons giving F$^{+}$ (e$_O^{••}$) or F ($V_X^-$) centers while holes are temporarily immobilized in the vicinity of Er$_{Sn}^N$ giving [Er$_{Sn}^N$-h$^•$] entities. Alternatively, holes can also be trapped in the Er$_{Sn}$ site due to its net negative charge, giving [Er$_{Sn}$-h$^•$] [51]. The glow curve obtained at a heating rate of 3 K s$^{-1}$ for the (Er, F)
co-doped SnO$_2$ crystals were deconvoluted into 4 first-order peaks by the Glow Fit computer program (Figure 8b). The heavily F-doped SnO$_2$ system showed 3 types of traps [18]. The figure of merit (FOM), a parameter describing the quality of fitting, was calculated [24]. The values of kinetic parameters of the glow curve of (Er, F) co-doped SnO$_2$ at a heating rate of 3 K s$^{-1}$ were calculated by GCD method, Chen’s formulae, Grossweiner analysis, and Kivits Hagebeuk analysis and are presented in Table 2 [52–54]. The variation in TL intensities for (Er, F) co-doped SnO$_2$ nanocrystals on exposure to UV light (using a 125-W high vapor pressure mercury lamp) for 5, 10, and 15 min at a linear heating rate of 3 K s$^{-1}$ are shown in the inset of Figure 8a. The intensity of the glow peaks decreased and shifted towards higher temperatures with UV irradiation time. This effect is sometimes referred to as ‘radiation damage’ in the literature [55]. This type of behavior is quite opposite to that of the heavily F-doped SnO$_2$ system, where the intensity of the glow curves increased on exposure to UV irradiation.

![Image](a) TL glow curve of (Er, F) co-doped SnO$_2$ (blue circles) and Er-doped SnO$_2$ (red stars). Inset shows TL glow curves of (Er, F) co-doped SnO$_2$ recorded at 3 K s$^{-1}$ after irradiating it with UV light for 0, 5, 10, and 15 min. (b) Glow-fitting curve (black solid line) and deconvoluted peaks of (Er, F) co-doped SnO$_2$ obtained by the Glow Fit program on the experimental TL curve (red circles).

**Figure 8.** a) TL glow curve of (Er, F) co-doped SnO$_2$ (blue circles) and Er-doped SnO$_2$ (red stars). Inset shows TL glow curves of (Er, F) co-doped SnO$_2$ recorded at 3 K s$^{-1}$ after irradiating it with UV light for 0, 5, 10, and 15 min. b) Glow-fitting curve (black solid line) and deconvoluted peaks of (Er, F) co-doped SnO$_2$ obtained by the Glow Fit program on the experimental TL curve (red circles).

**Table 2.** Summary of the trap depth (E) values, frequency factor (S), and FOM of glow curve 1 of the (Er, F) co-doped SnO$_2$ fitted by various methods.

<table>
<thead>
<tr>
<th>TL deconvoluted peak</th>
<th>$T_m$ (K)</th>
<th>Trap depth (eV)</th>
<th>$S$ (s$^{-1}$) (GCD)</th>
<th>FOM %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Glow curve shape methods</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Chen [52]</td>
<td>Grossweiner et al. [53]</td>
<td>Kivits and Hagebeuk [54]</td>
</tr>
<tr>
<td>TL1</td>
<td>467</td>
<td>0.89</td>
<td>0.94</td>
<td>0.87</td>
</tr>
<tr>
<td>TL2</td>
<td>493</td>
<td>0.84</td>
<td>0.90</td>
<td>0.84</td>
</tr>
<tr>
<td>TL3</td>
<td>524</td>
<td>0.71</td>
<td>0.77</td>
<td>0.71</td>
</tr>
<tr>
<td>TL4</td>
<td>591</td>
<td>0.55</td>
<td>0.60</td>
<td>0.55</td>
</tr>
</tbody>
</table>

The room-temperature ferromagnetism observed in nanosized ZnO, SnO$_2$, and TiO$_2$, which are otherwise diamagnetic, has created immense interest in understanding the interactions between the surface OVs
 existing in these systems [7,23]. The room-temperature magnetization of (Er, F) co-doped SnO\textsubscript{2} showed significant hysteresis at room temperature, possibly from a ferromagnetic ordering, as presented in Figure 9. The coercivity was found to be \(\sim 180\) Oe at room temperature. Ferromagnetism might be missing from the exchange interactions between the unpaired electron spins arising from defects and OVs at the surface of the nanocrystals. It has been suggested that room-temperature ferromagnetism results from the magnetic coupling between V\textsuperscript{0}\textsuperscript{+} centers at the surface of the nanoparticles [23,56,57]. The ferromagnetic behavior of Er-doped SnO\textsubscript{2} is slightly different from that of (Er, F) co-doped SnO\textsubscript{2}. After showing a small hysteresis in low fields, the magnetization of (Er, F) co-doped SnO\textsubscript{2} increased linearly in higher fields. This type of linear behavior might be attributed to the magnetic moment associated with the conduction electrons [58].

![Figure 9. Plot of magnetization versus magnetic field of (Er, F) co-doped SnO\textsubscript{2} (blue circle) and Er-doped SnO\textsubscript{2} (red stars).](image)

### 4. Conclusion

The interaction of the hole created by the doping of an \(f\)-block element with the vacancies generated due to heavy doping of fluoride in SnO\textsubscript{2} nanocrystals has been studied for the first time. Widening of the band gap due to the combined effect of quantum confinement and Moss–Burstein effect occurred with the co-doping of SnO\textsubscript{2}, yielding a value of 4.18 eV. The presence of huge OVs that are highly disordered is observed in co-doped samples. The presence of multiphonon interactions, which were earlier reported only in SnO\textsubscript{2} nanostructures such as nanowires and nanorods, are observed in the Raman and IR spectra of (Er, F) co-doped SnO\textsubscript{2} nanocrystals exhibiting spherical morphology. Pore size analysis revealed significant porosity in co-doped samples with mean pore diameter of 25.82 nm. The samples also showed increased thermal stability over a wide range of temperature (50–900 °C). Strong green luminescence observed in PL of (Er, F) co-doped SnO\textsubscript{2} nanocrystals suggests their potential use in optoelectronic devices such as LEDs. Additionally, the co-doped samples without any external irradiation exhibited glow curves in the TL spectra, signifying the presence of deeper traps in the system. Irradiating the co-doped samples with UV light for different intervals of time resulted in the resolution of the glow curves. (Er, F) co-doped SnO\textsubscript{2} nanocrystals are quite environmentally friendly, robust, and relatively simple to fabricate in different sizes in larger quantities and therefore can be used as active temperature and UV light sensors in places where direct contact sensors fail. The co-doping approach has stabilized ferromagnetism at room temperature.
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