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Original Research Article

Structural and optical characterization of Sm³⁺ ions and CdTe crystallites doped in silica matrices using sol-gel method

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ABSTRACT
In this study, Sm³⁺ ions and CdTe crystallites doped in silica matrices were prepared using the sol-gel method. The change in phase is observed to significantly boost the samarium ion emission intensities. $CdTeO_3$ phase is produced by heating sol-gel glasses containing CdTe crystallites to a temperature of around 800°C for about 10 hours in the absence of oxygen. Tellurium evaporation results in high porosity, which opens up pores for atmospheric oxygen to diffuse through, resulting in oxygenated CdTe crystallites. It is possible to explain the increased emission of Sm³⁺ ions by the energy transfer from oxygenated CdTe nanocrystallites.

1. Introduction

Sol-gel silica matrices may be regarded as excellent hosts for II-VI semiconductors and rare earth ions [1]. ZnS, ZnSe, CdTe, and other materials can be included into the glasses at low temperatures with a certain concentration [2]. Due in large part of their employment in IR sensing applications, CdTe has emerged as the well-established photonic material [3]. It has gained considerable interest as the potential material for the synthesis of solar cells [4]. Fast operating devices appropriate for optical signal processing are also made possible by significant photorefractive effect seen in CdTe.

For the purpose of producing high-quality polycrystalline and epitaxially formed thin film of Zn and Cd chalcogenides for application in several luminous devices, experiments have been conducted. By enhancing the level of crystalline and minimizing effect of dislocations via heating, these chalcogenides' quality is enhanced. Chalcogenides may, however, undergo changes in characteristics when heated in air due to reactions with atmospheric gases, particularly oxygen. The fundamental reason for the surprising differences found in the photoconducting and optical properties was reported to be oxygen chemisorption [5]. These chalcogenides can be added by wet chemistry to sol-gel glasses to more effectively decrease this effect.

According to earlier study, oxidation can begin as low as 100°C. Additionally, there aren't many works that combine the solgel and oxygenation processes. The current work demonstrates that using the sol-gel technique can postpone oxygenation of amorphous cadmium telluride by up to 600°C. One of the greatest ways to determine phases is using X-ray diffraction. Because trivalent samarium ions glow well in the visible and infrared spectrum, spectroscopic studies of these compounds have drawn a lot of attention. Due to the possible technological applications, it is crucial to comprehend the optical characteristics of Sm³⁺ ions. Here, we also use judd-ofelt analysis to examine the impact of oxygenated CdTe phases on samarium ion enhanced fluorescent emission.

2. Experimental

Sol-gel method was used to create silica glass that was codoped with Sm³⁺/CdTe [6]. The procedure uses ethanol for hydrolysis and TEOS as a precursor. To create CdTe, $C_4H_6CdO_4$ and Na_2TeO_3 were utilised in the synthesis. Sm³⁺ ions were added to the matrix using samarium nitrate. To evaluate the structural evolution, the samples were annealed in the open atmosphere at 50°C, 200°C, 500°C, and 800°C temperatures. In order to analyse the optical properties, the emission spectrum as well as the absorption spectrum were collected. The various vibrational modes were allocated from the FTIR spectra of the sample after it had undergone heat treatment at various temperatures. Using a Brooker diffractometer, the X-ray diffraction spectra of the prepared samples were captured at different temperatures.

3. Results and discussion

Absorption spectrum: The absorption spectrum of the sample is depicted in Figure 1. It exhibits six absorption bands centred at 344 nm , 361 nm , 373 nm, 401 nm ,415nm , 463 nm, 478 nm wavelengths due to the $^6H_{5/2} \rightarrow {}^4H_{9/2}$, $^4D_{3/2}$, $^4L_{17/2}$, $^4P_{3/2}$, $^4I_{3/2}$, $^4M_{15/2}$ transitions, respectively.

Judd-Ofelt analysis: The relationship between the molar extinction coefficient (ε) and the energy of the wave number

transition (ν) may be used to represent the oscillator strength (*f*) via equation $f_{exp} = 4.32 \times 10^{-9} \int \varepsilon \nu \, d\nu$ .. The three Judd-Ofelt parameters, viz. Ω_2, Ω_4 and Ω_6 are assessed using the J-O theory based on the oscillator strengths of distinct absorption bands of these glasses.

$$f_{ed} = \frac{\nu}{(2J+1)} \left[\frac{8\pi^2 mc}{3h} \frac{(n^2+2)^2}{9n} \right] \sum_{\lambda=2,4,6} \Omega_\lambda \left\langle \psi J \left| U^\lambda \right| \psi' J' \right\rangle^2$$

where (2*J*+1) is the degeneracy of the ground state, ν is the mean energy of the $\left| \psi J \right\rangle \rightarrow \left| \psi' J' \right\rangle$ transition. U^λ is an operator corresponding to the unit tensor of rank λ and Ω_λ's may be regarded as the J-O parameters. These parmaters were determined as: $\Omega_2 = 37.51$, $\Omega_4 = 0.21$ and $\Omega_6 = 0.23 \times 10^{-20}$ cm^2 having the quality-factor of the order of unity. Table 1 contains a list of these Ω_λ's. The three Judd-Ofelt parameters, which vary between hosts, hold valuable knowledge regarding crystal's potential field and how it affects ionic function. Ω_2 connects both the long-range effects and the covalency and/or structural alterations that occur close to the Sm^{3+} ion. For sample B, a strong bonding between metal-ligands may be seen by the big value of the Ω_2 intensity parameter. The covalancy of rare-earth ion positions affects the self-emission likelihood, which is based on values of Ω_4 and Ω_6. By combining with CdTe nanoparticles, the samarium ions' emission intensities are observed to be significantly boosted.

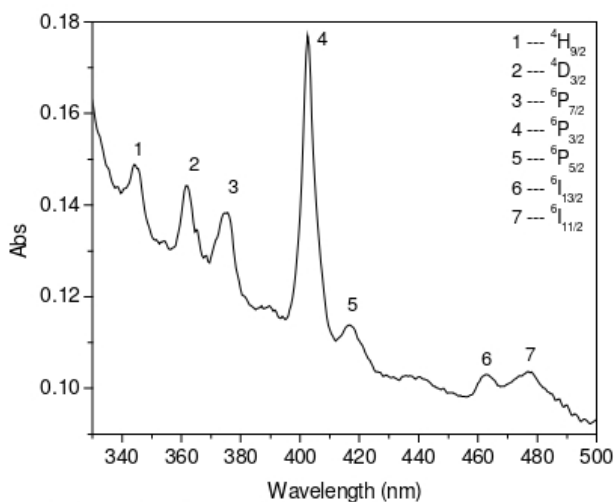**Figure 1.** Absorption spectrum.

Table 1. FTIR bands

IR peak (in cm^{-1})	Assignments
3000 – 3500	Stretch of O-H bonding
2932	Stretch of C-H bonding
1241	Stretch in cyclic structure of Si-O-Si asym.
1076	Stretch in cyclic structure of Si-O-Si asym.
985	Stretch of Si-O(H)
921	Nonbridging broken Si-O
775	Bending of Si-O-Si asym.
476	Bending of O-Si-O asym.

FTIR analysis: When TEOS is hydrolyzed, Si-OH groups are produced. These Si-OH groups then begin to interact with one another in a process known as polycondensation, which results in a three-dimensional silica network. Figure 2 displays

the sol-gel silica matrix FT-IR spectra. In Table 1, absorption bands' assignments are listed. The polymerisation of Si-OH bonding, which results in formation of the Si-O-Si bonding in the newly formed structure, is attributed to the bands at 1236 and 1077 cm^{-1}. The appearance of a Si-O bonding at 921 cm^{-1} was found in gels heated to 200°C. Researchers may use the band at 960 cm^{-1} to examine the polymerization of Si-OH compounds. Since wave number is, in general, related to potency of the Si-OH bonding, this band's position grows as the gel's degree of inter-locking. Gels and glass are also known to exhibit wave number variation up to 985 cm^{-1}. There is a spectroscopically discernible quantity of broken down Si-O bonding in the silica matrix that possess a freedom for creating a peak at 921 cm^{-1} in gel-derived silica glasses. New silicate anions create new bands if the formation of Sm-O-Si bonding takes place. By symmetrically stretching Si-O bonding in SiO$_4$ tetrahedral with various oxygen contents and coordinating with Sm^{3+}, the peak at 940 cm^{-1} is created. Due to dissolution of the Si-O-Si bonding, the oxygen bonded to Sm-O-Si may be regarded as non-bridging oxygen (NBO). The band at 940 cm^{-1} is caused by two NBO molecules of SiO4 that coordinate to the europium. The strength of the band resulting from the Si-OH stretched vibration and the appearance of adsorbed water decreased with increasing temperature.
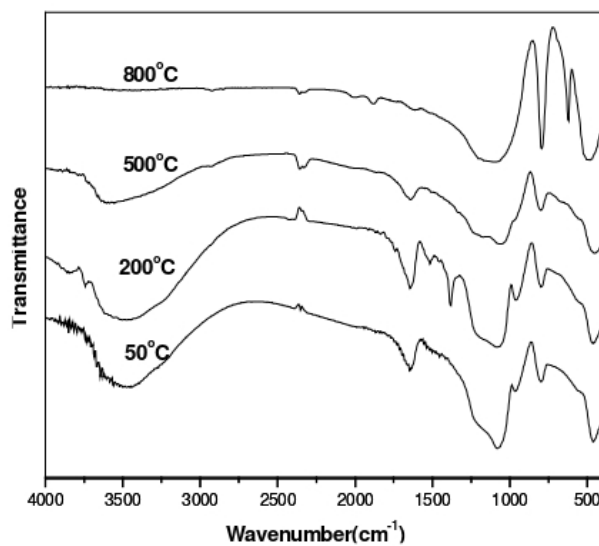

Figure 2. FTIR spectrum at 50°C, 200°C, 500°C, and 800°C temperatures

XRD analysis: At 200°C, 500°C, and 800°C, the samples of CdTe were annealed in open atmosphere. The samples were heated in a sealed furnace for 5 hours for 200°C, 500°C, and 10 hours for 800°C, respectively, before being allowed to cool gradually to ambient temperature. Figure 3 displays the XRD spectra of the samples after thermal treatment at 500°C and 800°C. There are no noticeable peaks in the XRD spectra at 500°C. However, the sample's crystalline character is clearly visible at 800°C. The JCPDS data comparison shows that Cadmium Tellurium Oxide is formed (CdTeO$_3$). Given that the sample was air annealed, this outcome is predictable. Similar outcomes were found for the oxidation of CdSe and CdTe in the respective oxide forming without producing any CdO [2]. On heat treatment, the CdTe phase develops at the expense of the thermally produced CdTeO$_3$ phase. Tellurium, which is

extremely volatile, may also prevent CdTe phase development. The stiff silica matrix is responsible for the high oxygenation temperature.
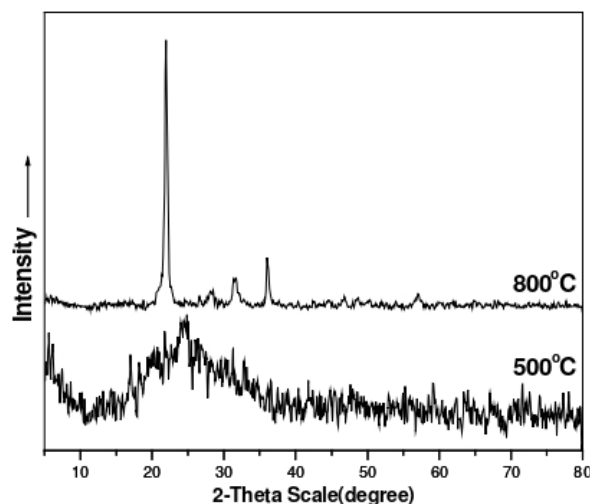

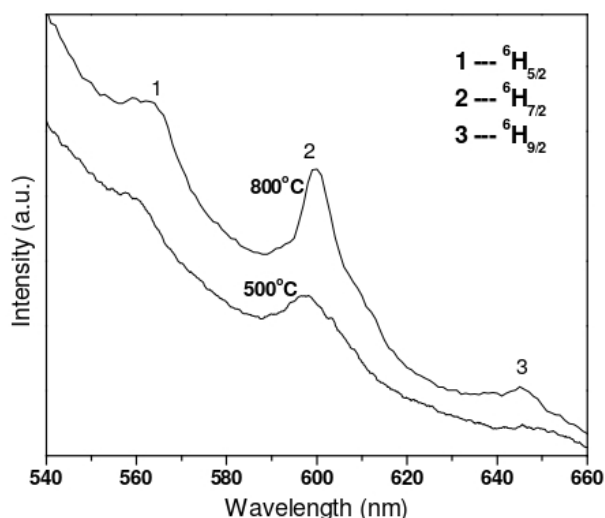**Figure 3.** XRD spectra at 500°C and 800°C

Figure 4. Fluorescence spectra at 500 and 800°C

Structural analysis: Numerous writers [2] have explained the oxygen migration in air annealed $A^{II}B^{VI}$ type semiconductors. Heiba et al. [7] provided an explanation of structural properties of the oxygen migration in lattice of the thermally heated CdTe compound. Weight loss is observed when cadmium telluride is heated in air, and this is attributable to the extremely volatile Te evaporating [8]. Te sublimation leaves voids in the lattice that allow oxygen to seep into the lattice. Oxygen can be accommodated in the octahedral interstitial sites of CdTe that has been annealed at 800°C. This finding demonstrates that oxygen transport through the semiconductor lattice of type II-VI is possible. The absorption of oxygen in the lattice can result in the modification of structure of the band gap, which alters the physical characteristics. One may observe that oxygen occupancy depends on both the annealing temperature as well as the length of annealing time and rises on raising the temperature

and the quantity of CdTeO^3. While Te atoms, have a decreasing relative occupancy, the comparative occupancy of Cd atoms is nearly same for all temperatures.

Fluorescence studies: Figure 2 displays the samples' fluorescence spectra. The fluorescence spectrum display three bands with centres roughly at 556 nm, 594 nm, and 641 nm, which correspond to the excited states of $^6H_{5/2}$, $^6H_{7/2}$, and $^6H_{9/2}$ of the Sm^{3+} ion, respectively. For the strongest 594 nm transition, the branching ratios at 500°C ($\beta = 0.60$) and 800°C ($\beta = 0.68$) were found. The transfer of energy from the changed CdTe state to the rare earth ion is what is responsible for the improvement in emission spectra.

4. Conclusions

Sm^{3+} ions and CdTe crystallites doped in silica matrices have both been generated via the sol-gel technique. The change in phase is observed to significantly boost the samarium ion emission intensities. CdTeO$_3$ phase is produced by heating sol-gel glasses containing CdTe crystallites to a temperature of around 800°C for about 10 hours in the absence of oxygen. Tellurium evaporation results in high porosity, which opens up pores for atmospheric oxygen to diffuse through, resulting in oxygenated CdTe crystallites. It is possible to explain the increased emission of Sm^{3+} ions by the energy transfer from oxygenated CdTe nanocrystallites.

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