



Solid state speciation of uranium and its local structure in Sr₂CeO₄ using photoluminescence spectroscopy

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ABSTRACT

An effort was taken to carry our speciation study of uranium ion in technologically important cerate host Sr₂CeO₄ using time resolved photoluminescence spectroscopy. Such studies are not relevant only to nuclear industry but can give rich insight into fundamentals of 5f electron chemistry in solid state systems. In this work both undoped and varied amount of uranium doped Sr₂CeO₄ compound is synthesized using complex polymerization method and is characterized systematically using X-ray diffraction (XRD), Raman spectroscopy, photoluminescence spectroscopy and scanning electron microscopy (SEM). Both XRD and Raman spectroscopy confirmed the formation of pure Sr₂CeO₄ which has tendency to decompose peritectically to SrCeO₃ and SrO at higher temperature. Uranium doping is confirmed by XRD. Uranium exhibits a rich chemistry owing to its variable oxidation state from +3 to +6. Each of them exhibits distinct luminescence properties either due to f-f transitions or ligand to metal charge transfer (LMCT). We have taken Sr₂CeO₄ as a model host lattice to understand the photophysical characteristics of uranium ion in it. Emission spectroscopy revealed the stabilization of uranium as U(VI) in the form of UO₆⁶⁻ (octahedral uranate) in Sr₂CeO₄. Emission kinetics study reflects that uranate ions are not homogeneously distributed in Sr₂CeO₄ and it has two different environments due to its stabilization at both Sr²⁺ as well as Ce⁴⁺ site. The lifetime population analysis interestingly pinpointed that majority of uranate ion resided at Ce⁴⁺ site. The critical energy-transfer distance between the uranate ion was determined based on which the concentration quenching mechanism was attributed to electric multipolar interaction. These studies are very important in designing Sr₂CeO₄ based optoelectronic material as well exploring it for actinides studies.

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1. Introduction

In recent days, the development of luminescent material with three primary colors is demanding in the field of display devices [1,2]. Highly luminescent materials with less power consumption are most demanding. Y₂O₃:Eu³⁺ emits in Red-region and Y₃Al₅O₁₂:Tb³⁺, Y₃Al₅O₁₂:Ce³⁺, emits in green region and find their application in various areas [3,4]. But the conventional blue-emitting sulfides doped with either rare earth or transition metal did not find many applications due to chemical instability and sensitivity to moisture. It is more difficult to find a suitable blue phosphor because of the required wide band gap. Thus, there is persistent efforts are being made to develop efficient and chemically stable blue luminescent materials [5–7]. Danielson et al. has found the ternary oxide molecule Sr₂CeO₄ by combinatorial chemistry method which shows blue luminescence [8]. The structure comprises of one-dimensional chain of edge-sharing CeO₆ octahedron separated by Sr atoms and it has emission peak which peaks at 485 nm; ascribed

to the charge-transfer transition Ce⁴⁺–O²⁻. Sr₂CeO₄ phosphor has been widely studied because of its stability in atmosphere and capability of showing emission in near white region for applications in LEDs and displaying devices [9].

Many methods have been adopted for the synthesis of Sr₂CeO₄. The conventional solid state reaction method which requires high energy and the products obtained were highly crystalline with non-uniformity [10–12]. The soft chemistry method [13–21] requires less energy and the products formed were found to be uniform and of nano size which is very essential to have good optical property. We have already exhaustively studied the blue-white light emitting Sr₂CeO₄ and red emitting Sr₂CeO₄:Eu³⁺ nanoparticles which were prepared by polymeric precursor route [22]. Though there are many literature on various lanthanide ion (Nd³⁺, Sm³⁺, Eu³⁺, Dy³⁺, Yb³⁺) doped Sr₂CeO₄ [11,13,14,23,24], but to the best of our knowledge, there is no study with uranium doped Sr₂CeO₄. Compared to 4f electron in lanthanides; 5f-electrons are relatively less shielded by outer lying electrons. As a result they are more perturbed by local crystal field which results in broad emission and absorption spectrum. Oscillator strength of 5f-5f transition is relatively larger than in iso-electronic lanthanide ion. Uranium is the most

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studied actinide as it is not so radioactive and available naturally. It can exist in different oxidation states, such as U(III), U(IV), U(V) and U(VI). Each oxidation state has a characteristic optical spectroscopic fingerprint. Hexavalent Uranium depending on the synthesis conditions can have different molecular structure leading to UO_4^{2-} , UO_6^{6-} or UO_2^{2+} species. The environmental impact of any metals ion depends on its concentration and more precisely its speciation.

Uranium in all the oxidation state shows luminescence properties and stabilizes under different conditions. As such most of the studies depicted that uranium stabilizes in +3, +4, +5 state in single crystal whereas U (+6) stabilizes in polycrystalline powder [25]. There are many studies on stabilization of various oxidation states of uranium and its luminescence properties in solid matrices as mostly reported by our group from Bhabha Atomic Research Centre [25–32]. UO_2^{2+} emits in green region of visible spectrum, which is due to ligand to-metal charge transfer (LMCT) emission in solution as well as in solid state [25]. Such studies are relevant not only from nuclear perspective but also from technological application in the field of photocatalysis [33], bioremediation [34], and chemosensor [35].

The remarkable blue luminescence and high stability of Sr_2CeO_4 prompted us to explore the luminescence properties of uranium doped matrix. In the present study, $\text{Sr}_{2-x}\text{U}_x\text{CeO}_4$ ($x = 0, 0.005, 0.008, 0.01, 0.015, 0.02$) was synthesized by complex polymerization method at low temperature using urea as complexing agent, characterized by X-ray Diffraction analysis (XRD), Raman spectroscopy and scanning electron microscopy (SEM) and the luminescence properties were studied using TRPL spectroscopy. This study gave idea about local site occupancy and symmetry, valence state etc.

2. Experimental

2.1. Synthesis

$\text{Sr}_{2-x}\text{U}_x\text{CeO}_4$ ($x = 0, 0.005, 0.008, 0.01, 0.015, 0.02$) was synthesized by complex polymerization method employing urea as complexing agent and ethylene glycol as polyesterifying agent.

The starting reactants used were SrCO_3 (99.95% purity, M/s Alfa Aesar, Germany), urea (99.5%, M/s Sisco Research Laboratory Pvt Ltd, Mumbai), U_3O_8 (99.999% purity supplied by NFC, Hyderabad), $\text{Ce}(\text{NO}_3)_3 \cdot 5.6 \text{H}_2\text{O}$ (99.5% purity supplied by M/s Across Organics, Mumbai) and ethylene glycol (99.0%, M/s Thomas Baker, Mumbai). Selectipur HNO_3 (M/s Merck Ltd, Mumbai) were used as solvent and NH_3 solution (M/s Chemco Fine Chemicals, Mumbai) was used for pH adjustment. Initially, SrCO_3 was brought to solution with dil HNO_3 . $\text{Ce}(\text{NO}_3)_3 \cdot 5.6 \text{H}_2\text{O}$ was separately dissolved in 1 M HNO_3 (aq.) and the Ce content in the resultant solution was determined using potentiometric method developed for plutonium by Drummond et al. [36]. Ce solution containing required amount of Ce for the synthesis of Sr_2CeO_4 was added to the Sr solution. For the doped samples required amount of U_3O_8 dissolved in HNO_3 was also added. Excess amount of fuel i.e. urea was added and pH adjusted to 2–2.5. Then ethylene glycol was added upon stirring on a hot plate at 100 °C. At the point of gel formation, the beakers containing respective solutions were kept in preheated furnace at 500 °C for 3 h. Then, the precursors were ground, pelletized and kept at 850 °C for 20 h and latter at 1000 °C for 20 h in a furnace under static air. The color of pure Sr_2CeO_4 was found to be grayish white but the doped samples were yellowish in color. All the metal present in the solution are in nitrate form and acts as oxidant. We have taken urea as fuel and the (Fuel/Oxidant) ratio was maintained to 1. The mass ratio between urea and ethylene glycol was fixed at 6:4.

2.2. Characterisation

(XRD) using a STOE theta–theta X-ray diffractometer with graphite monochromatic $\text{Cu K}\alpha$ radiation ($k_\alpha = 0.15406 \text{ nm}$). The 2θ range covered was from 10° to 60°.

Sr_2CeO_4 was also characterized by Raman spectroscopy using micro/macro-Raman spectrometer (Model: LABRAM-1, France) with 488 nm excitation line of an Ar + ion laser with 14 mW power. The scattered Raman signals were collected in the back scattering geometry using a single monochromator spectrometer equipped with a Peltier-cooled CCD detector. The excitation laser line was focused on the flat surfaces of sample pellet of diameter 8 mm using optical microscope (Olympus BX-40, 50_x objective lens). The procedure for calibration and recording of spectra were carried out as per the procedure given earlier [37].

SEM images were recorded on SNE 4500 Mini SEM instrument. An Edinburgh CD-920 unit was used for recording the PL data, which is equipped with M 300 monochromators. Data acquisition and analysis were done by using F-900 software provided by Edinburgh Analytical Instruments, UK. Emission spectra for a particular sample was recorded with a Xenon flash with a frequency of 100 Hz. Multiple Scans (at least five) were taken to minimize the fluctuations in peak intensity and maximize S/N ratio. Fluorescence lifetime measurements were based on well established Time-correlated single-photon counting (TCSPC) technique.

3. Results and Discussion

3.1. Phase Purity and Structural Characterisation: XRD and Raman Spectroscopy

The XRD taken for the synthesized Sr_2CeO_4 heated at 850 °C showed mixture of peaks from SrCO_3 , CeO_2 and SrCeO_3 as shown in Fig. 1. But heating at high temperature at 1000 °C, all the peaks corresponded to the peaks of Sr_2CeO_4 (PCPDF: 50-0115) without any extraneous peaks, which confirmed the pure phase formation of Sr_2CeO_4 . Similarly, all the XRD pattern of U-doped samples (Fig. 2) were compared with that of pattern obtained for Sr_2CeO_4 heated at 1000 °C.

The room temperature Raman spectra of Sr_2CeO_4 prepared at 1000 °C is shown in Fig. 3. There are seven peaks in the spectrum at 107.8, 144.8, 216.9, 285.2, 384.0, 464.7, 553.22 cm^{-1} respectively. The band at 553 cm^{-1} is attributed to the vibration of Ce–O₁ [38] in Sr_2CeO_4 . Two strong Raman bands at 286 and 385 cm^{-1} can be attributed to the stretching modes of the Ce–O₂ and Ce–O₁ in CeO_6 octahedra. The contribution of Ce–O₂ bonds is more intense than that of Ce–O₁ bonds which induces the charge transfer [38] in Sr_2CeO_4 . O^{2-} – Ce^{4+} charge transfer induces excellent blue luminescence in this particular material. Though it is still only

speculative in nature and not confirmatory as the exact reason for luminescence in this material from Ce^{+4} is yet to be understood.

The Raman shift at 463 cm^{-1} also implies presence of trace amount of CeO_2 as it corresponds to F_{2g} band of CeO_2 [39]. But there are no peaks at 1073 cm^{-1} ascribed to symmetric stretching mode of SrCO_3 which confirms the formation of pure Sr_2CeO_4 phase.

3.2. SEM Analysis

The microstructure of the powder samples of Sr_2CeO_4 heated at 500 °C for 3 h 1000 °C for 20 h and the precursor of $\text{Sr}_{1.995}\text{U}_{0.005}\text{CeO}_4$ heated at 1000 °C for 20 h were studied and shown in Fig. 4a–c. The particle sizes were not uniform and regular at 500 °C and it started getting agglomerated with temperature as shown in Fig. 4(b). The image taken for $\text{Sr}_{1.995}\text{U}_{0.005}\text{CeO}_4$ heated at 1000 °C for 20 h shows development of rod like structure which could be due to the effect of uranium doping.

3.3. Uranium Oxidation State and Coordination Geometry: Photoluminescence Emission Spectroscopy

Fig. 5a depicts the excitation spectrum of pristine Sr_2CeO_4 . The spectrum displayed a broad band around 325 nm attributed to oxygen to cerium(IV) charge transfer. Fig. 5c shows the emission spectrum of Sr_2CeO_4 sample synthesized in our lab by complex polymerization

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