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Speciation and site occupancy of uranium in strontium orthosilicate by photoluminescence and X-ray absorption spectroscopy: A combined experimental and theoretical approach

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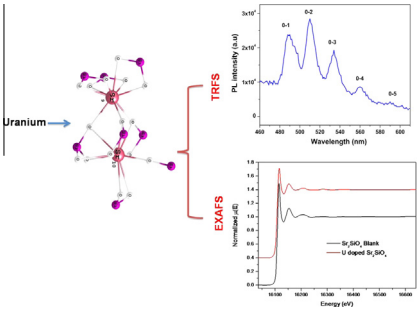
HIGHLIGHTS

- Uranium stabilizes as UO_2^{2+}.
- PL is characteristic of distorted environment for UO_2^{2+}.
- Majority of UO_2^{2+} occupy 9-coordinated Sr sites.
- DFT calculations also supported the experimental findings.

GRAPHICAL ABSTRACT



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ABSTRACT

Identifying the oxidation state and coordination geometry of radioactive element like uranium is important to fully understand its toxicology and other harmful effect in environment. Strontium orthosilicate is taken as a model compound for that. Strontium silicate doped with 1.0 mol% of U has been synthesized using sol–gel method and characterized using X-ray diffraction (XRD), time resolved fluorescence spectroscopy (TRFS) and extended X-ray absorption fine structure (EXAFS). Uranium exhibits multiple oxidation state and each one of them is having characteristics luminescence is an interesting dopant from structural point of view. TRFS is used to investigate the oxidation state and coordination behavior of uranium in Sr_2SiO_4. From TRFS measurement it was observed that uranium stabilizes in +6 oxidation state in the form of uranyl ion. Based on luminescence lifetime and EXAFS studies it was inferred that uranyl is stabilized on both 9- and 10-coordinated strontium polyhedra but majority occupies relatively asymmetric 9-coordinated Sr sites. This is further confirmed using theoretical measurement.

1. Introduction

Alkaline earth silicates are found to a very good host material for lanthanide doping because of various properties such as (a) similarity between the ionic radius of the alkaline earth and the lanthanide ions (b) resistant to many chemicals and air exposure and can also be grown with low-cost techniques (c) stable crystal structure, good mechanical strength and high thermal stability provided by the tetrahedral silicate $(SiO_4)^{2-}$ group and (d) optical band gap is in the range of 4–7 eV and therefore these materials

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are characterized by good transmission properties in the visible part of the electromagnetic spectrum.

Silicate based inorganic host has been explored extensively in various aspect of solid state lighting. Some of the novel silicate based host with potential application are $NaScSi_2O_6:Eu^{2+}$, Mn^{2+} [1] which act as the effective phosphors for UV-LEDs, color-tunable $Ba_{1.55}Ca_{0.45}SiO_4:Eu^{2+}$, Mn^{2+} phosphors [2] which have great prospects for white light-emitting diodes applications and near UV-pumped green-emitting $Na_3(Y, Sc)Si_3O_9:Eu^{2+}$ phosphor [3] for white-emitting diodes.

In that context strontium orthosilicate is a well known luminescence host in phosphor industry. In developing white light emitting diodes (LEDs) Gallium nitride single crystal (GaN) coated with $Sr_2SiO_4:Eu^{2+}$ exhibits better luminous efficiency than that of commercially available InGaN coated with YAG:Ce [4]. It is an excellent host for lanthanide luminescence and lots of paper have recently been published in the literature pertaining to various lanthanide ions doped Sr_2SiO_4 as thermochromic material [5], as a dosimeter [6], in long afterglow phosphor [7], in IR detection [8] and in long lasting phosphorescence [9]. This is also an interesting host because of the fact that it consists of two different coordination for Sr ion; SrO_9 and SrO_{10}. Relatively it was reported that; 10-coordinated polyhedra is more symmetric than 9-coordinated polyhedra [10]. This fact we have explored on studying the site occupancy and optical behavior of lanthanide ion such as Sm^{3+}, Eu^{3+}, Eu^{2+}, and Dy^{3+} in Sr_2SiO_4 host [11–14]. Time resolved fluorescence spectroscopy (TRFS) is used to investigate the local environment and it was found that europium ion stabilizes at both 9- and 10-coordinated Sr^{2+} site whereas Dy and Sm stabilizes at 9-coordinated Sr^{2+} site. In all cases lanthanide ion stabilizes as trivalent species. Unlike lanthanide ion; first half of actinides exhibit multiple oxidation state and rich chemistry because there f-orbitals are much more diffused and get's affected by local environment. Among actinides; uranium exhibits various oxidation state such as 3+, 4+, 5+ and 6+. Each oxidation state has characteristic optical fingerprint. Moreover U(VI) depending on the synthesis conditions, can have different molecular structure leading to UO_4^{2-}, UO_6^{6-} or UO_2^{2+} species.

It was observed that, in case of the pyrophosphate [15], borophosphate [16] and yttrium borate matrices [17], uranium gets stabilized as uranyl (UO_2^{2+}), whereas, in case of the tetraborate [18] and zirconate [19] matrices, it was the octahedra uranate species, UO_6^{6-} that gets stabilized preferentially. Silicates based minerals are abundantly present in environment and it is possible that uranium get's accumulated through natural geologic or hydrologic Processes. Moreover, ceramic materials based on the structures of natural minerals draw attention as an alternative to glass for radioactive waste disposal. Ceramics excel glass with respect to chemical, radiation and thermal stability. Phosphates and silicates are presented in nature by the variety of minerals that can be potentially suitable for such purpose, for example monazite, langbeinite, kosnarite, whitlockite, pollucite etc. Because of the radioactivity and other toxicological effect associated with uranium it is imperative to understand the speciation of U to understand and predict the future migration behavior of U and to remediate contaminated soils and subsurface sediments. It is an important component of intermediate-level radioactive waste (ILRW) and the isotopes of this radionuclide contribute significantly to its local as well as global long-term dose.

In order to understand the coordination behavior and speciation of uranium in SiO_4^{4-} based matrix we have synthesized Sr_2SiO_4 using sol–gel chemistry. This is the first report on uranium speciation and coordination in Sr_2SiO_4.

The environmental impact of any metals ion depends on its concentration and more precisely its speciation. Time resolved fluorescence spectroscopy (TRFS) provides information on lifetime and spectral characteristic of species which allows extracting information on oxidation state of the species present and its spectral identity. This method may therefore provide information complementary to EXAFS spectroscopy. Since two types of strontium polyhedra exists in strontium silicate SrO_9 and SrO_{10}; the nature of site occupied by uranium in strontium silicate is also of interest. Through the present work we have made an attempt to address this issue by incorporating uranium in Sr_2SiO_4 and studying them by TRFS and Sr K-edge EXAFS spectroscopy. The experimental results were modelled using DFT calculations.

2. Experimental

2.1. Synthesis

All the chemicals used in the sample preparation were of AR grade and procured from Sigma Aldrich. The alkaline earth silicate samples were prepared via a sol–gel route using tetraethyl orthosilicate (TEOS) and strontium nitrate adopting the standard procedure [20]. Detailed procedure is schematically shown in the flow chart in Fig. S1 (Supplementary file). The final product obtained was a free flowing white crystalline powder. For preparation of 1.0 mol% uranium doped sample, appropriate quantities of uranyl nitrate, were added to the hydrolyzed TEOS solution.

2.2. Instrumentation

The phase purity of the prepared phosphors was confirmed by X-ray diffraction (XRD). The measurements were carried out on a STOE X-ray diffractometer equipped with scintillation counter and graphite monochromator. The diffraction patterns were obtained using monochromatic Cu-K_α radiation ($\lambda = 1.5406$ Å) keeping the scan rate at 1 s/step in the scattering angle range (2θ) of 10–60°. The $K_{\alpha 2}$ reflections were removed by a stripping procedure to obtain accurate lattice constants.

PL data were recorded on an Edinburgh CD-920 unit equipped with Xe flash lamp as the excitation source. The data acquisition and analysis were done by F-900 software provided by Edinburgh Analytical Instruments, UK.

The EXAFS measurements have been carried out at the Energy-Scanning EXAFS beamline (BL-9) in transmission mode at the INDUS-2 Synchrotron Source (2.5 GeV, 100 mA) at Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India [21]. This beamline operates in energy range of 4 keV to 25 keV. The beamline optics consist of a Rh/Pt coated collimating meridional cylindrical mirror and the collimated beam reflected by the mirror is monochromatized by a Si(1 1 1) ($2d = 6.2709$) based double crystal monochromator. The second crystal of DCM is a sagittal cylinder used for horizontal focusing. Three ionization chambers (300 mm length each) have been used for data collection in transmission mode, one ionization chamber for measuring incident flux (I_0), second one for measuring transmitted flux (I_t) and the third ionization chamber for measuring EXAFS spectrum of a reference metal foil (Mn foil in this case) for energy calibration. Appropriate gas pressure and gas mixture have been chosen to achieve 10–20% absorption in first ionization chamber and 70–90% absorption in second ionization chamber to improve signal to noise ratio. Rejection of the higher harmonics content in the X-ray beam is performed by detuning the second crystal of DCM. Minimum three scan is recorded for each sample and merged in later stage of data reduction to improve the signal to noise ratio. The absorption coefficient μ is obtained using the relation:

$$I_t = I_0 e^{-\mu x} \quad (1)$$

where, x is the thickness of the absorber.