

Photoluminescence, thermally stimulated luminescence and electron paramagnetic resonance studies of U⁶⁺ doped BaSO₄

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Abstract. U⁶⁺ doped BaSO₄ samples were synthesized by precipitation route. PL, TL and EPR investigations of γ and self α irradiated samples were carried out. PL spectra of these samples give structured broad band peaking around 518 nm with five vibronic bands centred around 498.4, 516.0, 533.7, 554.0 and 575.1 nm, respectively and the average frequency of symmetric stretching of O=U=O in the ground electronic state was found to be 674 cm⁻¹. Trap level spectroscopic studies of U doped BaSO₄ give glow peaks at 411, 488 and 512 K, respectively and their spectral characteristics are typical of UO₂²⁺ emission. EPR studies of γ -irradiated U⁶⁺:BaSO₄ sample have shown the presence of sulphonyl centred radicals like SO₄⁻ and SO₃⁻ in addition to OH[•], O₃⁻ and SH²⁻. TSL peaks at 411 and 488 K were correlated with thermal destruction of SO₄⁻ and SO₃⁻ radicals.

Keywords. EPR; TSL; PL; BaSO₄; uranium.

1. Introduction

Alkaline-earth sulphates with suitable dopants have played an important role in the development of thermoluminescent dosimeters (Vohra *et al* 1980; Shinde *et al* 1996) and offer a very fertile area for further studies to elucidate the thermally stimulated reactions resulting in luminescence. Actinide doped alkaline-earth sulphates are of special interest due to an array of defect centres that can be generated in these solids by self α and γ irradiation effects. Also structure of defect centres, their recombination on thermal stimulation resulting in luminescence, as well as possibility of stabilizing actinides in different valence states make them attractive host materials. Trap level spectroscopic studies of U⁶⁺/Pu⁴⁺/Am³⁺ doped CaSO₄/SrSO₄ using thermally stimulated luminescence (TSL) and electron paramagnetic resonance (EPR) were carried out earlier in our laboratory (Dalvi *et al* 1984; Seshagiri *et al* 1988, 1989; Kumar *et al* 1988; Natarajan *et al* 1989). Among these actinide elements, ²³⁸U due to its long-half life is not expected to give much of internal damage over a short period of time, whereas, in ²³⁹Pu/²⁴¹Am doped sulphates self irradiation effects were evident after short storage period of 5–10 days, resulting in the formation of variety of sulphonyl radicals due to high specific activity (1.6 × 10⁵-dpm and 7.8 × 10⁶-dpm, respectively) of these elements (Weast 1984). Uranium under normal conditions stabilizes in hexavalent state, though U³⁺, U⁴⁺ and U⁵⁺ states are possible under reducing conditions (Schreiber and Blazs 1982; Schreiber *et al* 1982). Hexavalent uranium depending on the synthesis conditions, can

have different molecular structure leading to UO₄²⁻, UO₆⁶⁻ or UO₂²⁺ species (E. 't Lam and Blasse 1980). In the present study, photoluminescence (PL), thermally stimulated luminescence (TSL) and electron paramagnetic resonance (EPR) investigations of freshly prepared and stored BaSO₄:U⁶⁺ samples were carried out with a view to understand the nature of defects formed by self/ γ irradiation and stabilization of uranium species under these conditions.

2. Experimental

U⁶⁺:BaSO₄ (1 mol%) samples were prepared by mixing equimolar (0.5 M) quantities of Ba(NO₃)₂ and (NH₄)₂SO₄ in solution. Appropriate amounts of high purity uranium as uranyl nitrate was added to Ba(NO₃)₂ solution before precipitation. Precipitate obtained was washed with quartz double-distilled water for 5–6 times to remove excess of ammonia present, dried and annealed at 1024 K for 2 h. XRD of annealed powders were recorded using STOE X-ray diffractometer. PL, TSL and EPR investigations of freshly prepared and stored (300 days) BaSO₄:U⁶⁺ were carried out. PL characterization was carried out using Edinburgh CD-920 fluorescence spectrometer. TSL studies were carried out on a home-built unit coupled to a personal computer by recording spectra of self and γ irradiated samples (dose in the range of 0.5–3 KGy). Trap parameters were calculated for BaSO₄:U⁶⁺ (dose = 1.5 kGy) sample by recording their TSL at different heating rates, e.g. 3, 2, 1 and 0.5 K/s. EPR spectra were recorded with Bruker ESP-300, X-band spectrometer, EPR and TSL spectra were correlated for deciding the stability of defect centres and their role in TSL.

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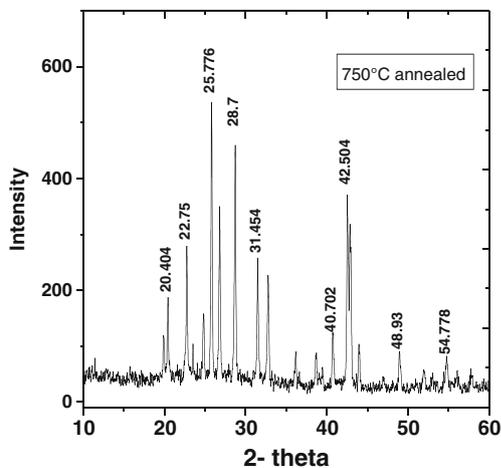


Figure 1. XRD pattern of $U^{6+}:\text{BaSO}_4$.

3. Results and discussion

3.1 XRD and PL investigations

XRD pattern of 1024 K annealed $U^{6+}:\text{BaSO}_4$ are given in figure 1. The diffraction pattern was in good agreement with reported data (JCPDS No. 80-0512) for BaSO_4 in orthorhombic barite phase (Salah *et al* 2009). PL emission of $U^{6+}:\text{BaSO}_4$ with $\lambda_{\text{ex}} = 260$ nm consisted of an intense signal peaking around 518 nm with overlapping vibronic structure (figure 2). This signal was de-convoluted and resolved into five bands positioned at 498.4, 516.0, 533.7, 554.0 and 575.1 nm. The band at 498.4 nm was attributed to zero phonon transitions from first excited level of triplet $^3\Pi_u$ to the ground state $^1\Sigma_g^1$ of UO_2^{2+} , while other bands are associated with transition from excited state to various higher vibronic levels in ground state (Ozoldova and Bohun 1980; Wang *et al* 2008a). The vibronic frequency of $\text{O}=\text{U}=\text{O}$ stretching obtained from difference in the position of successive emission bands was found to be 674 cm^{-1} . Thus, the green emission observed in fresh and stored $U^{6+}:\text{BaSO}_4$ samples was attributed to UO_2^{2+} . The stretching frequency of UO_2^{2+} in BaSO_4 host is quite less as compared to that observed (802 cm^{-1}) in UO_2SO_4 solid (Wang *et al* 2008b). In uranyl compounds, stretching frequency (ν_1) of uranyl ion was reported to be inversely proportional to the strength of interaction energy of U(VI) with co-coordinating ligands in equatorial plane. The stronger interaction between U(VI) and the equatorial ligands would result in weaker apical $\text{U}=\text{O}$ bond leading to lower stretching frequency (Wang *et al* 2004). Hexavalent uranium incorporated in solids can be present either as UO_2^{2+} , UO_6^{6-} or UO_4^{2-} species (De Hair and Blasse 1976; E. 't Lam and Blasse 1980) and can be distinguished from their PL emission. In U^{6+} doped CaSO_4 (870 K annealed samples), green emission of UO_2^{2+} was reported, which on annealing at 1170 K shifted to red region (660 nm) with concomitant decrease in green emission. This was attributed to formation of local uranate (CaUO_4) structure in the host

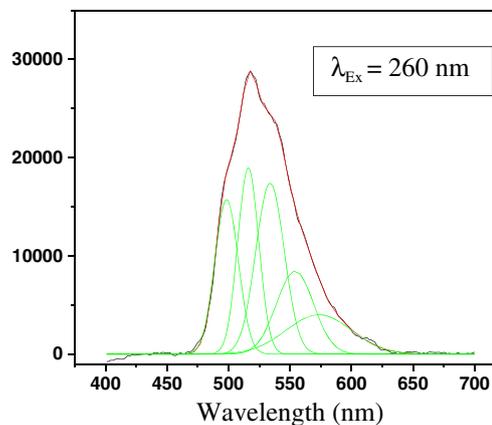


Figure 2. PL spectrum of $U^{6+}:\text{BaSO}_4$.

(Dalvi *et al* 1984). In our studies, such red shift was not observed in 1170 K annealed $U^{6+}:\text{BaSO}_4$ samples ruling out any possibility of UO_4^{2-} stabilization. PL spectra of UO_4^{2-} with tetrahedral structure has PL emission in orange-red region, while that of UO_6^{6-} (octahedral) and UO_2^{2+} species were reported in green region. However, UO_6^{6-} emission is different from that of UO_2^{2+} , where the number of vibronics is smaller and the progression is much more pronounced (De Hair and Blasse 1976; Lupei and Lupei 1979). The characteristic emission of UO_2^{2+} in green region is used in structural characterization of minerals and contaminated sediments (Geipel *et al* 2000; Wang *et al* 2005). The lifetime study carried out by following decay of 518 nm emission had shown a single lifetime ($\tau_1 = 43\ \mu\text{s}$) for UO_2^{2+} in unirradiated samples. Lifetime decreased marginally ($\tau_1 = 42.0\ \mu\text{s}$) in γ irradiated samples. This indicated only a single type of coordination around uranium in unirradiated and γ irradiated samples.

3.2 TSL studies

In TSL studies reported for U doped $\text{CaSO}_4/\text{SrSO}_4$, the low doping concentration of U (0.1%) was recommended (Kumar *et al* 1988; Seshagiri *et al* 1989) for optimization of TSL intensity. In the present study, concentration of U doping in BaSO_4 was increased to 1%, with a view to observe uranium self irradiation effects in terms of radical generation. TSL of U^{6+} doped BaSO_4 sample stored for 300 days gave a very weak and broad TSL signal suggesting that the population of defects produced by self irradiation was negligibly small. TSL of γ -irradiated (dose = 1.5 kGy) samples were recorded at different heating rates of 3, 2, 1 and 0.5 K/s. TSL spectra obtained with heating rate, $\beta = 2$ K/s, are given in figure 3. It consisted of glow peaks at 411 and 488 K along with a shoulder at 512 K. Trap depth was determined from the slope of the plot of $\ln(T_m^2)/q$ vs $1/T_m$. A least square programme was employed to get best fit of the trap depth value. The trap parameters viz. trap depth and frequency factor for glow peaks at 411 and 488 K were found to be $(0.975 \pm 0.12)\text{ eV}$, $1.1 \times 10^{11}\text{ s}^{-1}$

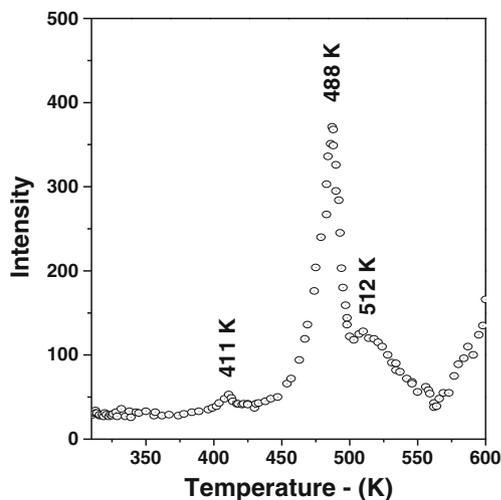


Figure 3. TSL of U^{6+} : $BaSO_4$ (heating rate - 2 K/s, γ -dose : 1.5 kGy).

and (1.3 ± 0.12) eV and $4.3 \times 10^{12} \text{ s}^{-1}$, respectively. For obtaining accurate trap parameters for 488 K peak, the 411 K peak was 'removed' by thermal treatment (heating to 400 K). Systematic gamma dose dependence of TSL glow peaks have shown that 411 and 488 K peaks saturate after a gamma dose of 0.8 and 2 kGy, respectively. TSL emission spectrum in 360–650 nm was studied using narrow band interference and transmittance filters. The narrow band interference filters used had a band pass of ± 20 nm. Emission observed around 480 and 520 nm indicated UO_2^{2+} ion to act as the emission centre.

3.3 EPR studies

EPR spectra of U^{6+} : $BaSO_4$ freshly prepared sample, after γ irradiation (dose = 1.5 kGy) and 'stored' (300 days) due to self α irradiation are shown in figure 4. EPR of self-irradiated sample generated with repetitive scans had shown a weak signal centred around $g = 2.0039$. This was attributed to SO_3^- radical (figure 4(a)). The formation of only SO_4^- and SO_3^- radicals by self α irradiation effects was reported earlier in Pu-doped $SrSO_4$ (Seshagiri *et al* 1988) and the yield of SO_3^- was reported to be substantially higher than that of SO_4^- radical. The observation of very weak SO_3^- signal in self irradiated U doped $BaSO_4$ is probably due to its low specific activity as compared to ^{239}Pu . EPR spectrum of γ irradiated sample (dose = 1.5 kGy) consisted of signals from different radicals (figure 4(b)). These radicals were identified by comparing their g values with the reported ones for γ -irradiated alkaline-earth sulphates (Seshagiri *et al* 1988). The radical signal having axial symmetry with $g_{\parallel} = 2.0328$ and $g_{\perp} = 2.0074$ was attributed to SO_4^- . The signal having orthorhombic symmetry with $g_1 = 2.0039$, $g_2 = 2.0027$, and $g_3 = 2.0015$ and its average g value (g_{av}) was found to be $-g_{av} = 2.0027$. This signal was identified as due to SO_3^- and the one with $g = 1.9963$ was due to SH^{2-} radical,

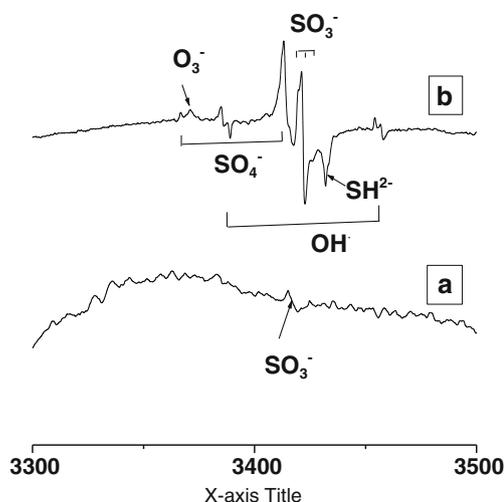
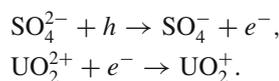


Figure 4. EPR of self irradiated (a) and γ irradiated (b) U^{6+} : $BaSO_4$ samples.

respectively (figure 4(b)). A broad signal around $g = 2.0353$ was attributed to O_3^- and a set of doublet centred around $g = 2.0028$ with hyperfine splitting $A = 69$ G was attributed to OH^\bullet radical. In present study, signals of UO_2^+ ($5f^1$) were not observed down to 77 K with a field sweep of 12 kG. However, reduction of U^{6+} to U^{5+} is well documented in γ irradiated alkali halides (Lupei *et al* 1976) and 77 K EPR spectrum of these samples showed U^{5+} signals in the field range (15–20 kG). Thus, the formation of UO_2^+ in γ irradiated U^{6+} : $BaSO_4$ cannot be ruled out. The stability of radiation induced radicals was monitored in the temperature range of 298–474 K and changes in signal intensity are shown in figure 5. γ -irradiated $BaSO_4:U^{6+}$ samples were heated using the pulsed thermal annealing technique, wherein sample was heated at desired temperature for 3 min, followed by rapid cooling to room temperature and EPR of cooled samples was recorded at room temperature. The temperature dependence of radical signal intensity suggested that thermal destruction of SH^{2-} , O_3^- and SO_4^- radicals occurs around 424 K. The destruction of SO_4^- in $BaSO_4$ host is analogous to that reported in U doped $CaSO_4/SrSO_4$ in the range 410–440 K (Seshagiri *et al* 1993).

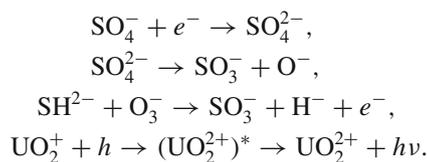
Based on TSL, PL and EPR observations, the following reaction mechanism are proposed for glow peaks.

On gamma irradiation:



411 K peak:

On heating at 400–425 K,



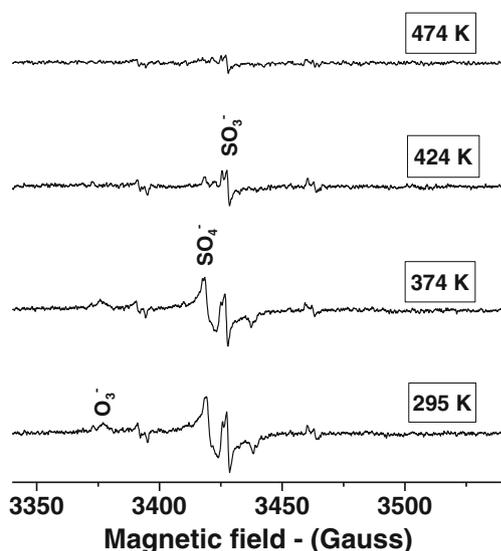
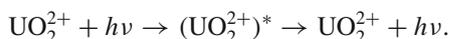
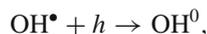
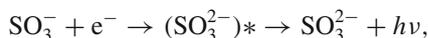


Figure 5. Temperature dependence of EPR of (a) γ irradiated and (b) $U^{6+}:\text{BaSO}_4$ samples.

Also, the intensity of SO_3^- and OH^\bullet radicals decreased significantly in 474 K annealed samples. This indicates that 488 K peak observed in TSL is related to SO_3^- radical destruction.

488 K peak:

On heating at 470–480 K,



EPR arises from the static nature of the traps while TSL occurs when electron/hole traps are ejected from charge centres. EPR experimental evidence suggested that the formation and stabilization of different radical ions in doped alkaline-earth sulphates were found to be both matrix and dopant dependent (De Hair et al 1976; E. 't Lam and Blasse 1980; Schreiber et al 1982; Dalvi et al 1984; Weast 1984; Natarajan et al 1989). In the present study, emission in the green region in $U^{6+}:\text{BaSO}_4$ was identified as due to UO_2^{2+} . The thermal destruction of SO_4^- and associated hole trapping at uranyl site was found to be responsible for TSL glow peak around 411 K. Further, the destruction of SO_3^- around 474 K was attributed to 488 TSL peak. The activation energy associated with SO_4^- traps is in agreement with the value of 0.95 ± 0.15 eV reported in CaSO_4 and SrSO_4 host with different dopants (Seshagiri et al 1989) and supports the proposition that the trap depth values are essentially independent of dopant incorporated in the alkaline-earth sulphate matrices and are typical of binding energy of 'hole' in SO_4^- radical.

4. Conclusions

Photoluminescence studies on U doped BaSO_4 showed a typical emission of UO_2^{2+} consisting of five vibronic bands having a frequency of 674 cm^{-1} due to symmetric stretching of $\text{O}=\text{U}=\text{O}$ in the ground electronic state. Self irradiation effects were found to be negligible in stored $U^{6+}:\text{BaSO}_4$. Thermal stabilities of SO_4^- , SO_3^- , O_3^- and SH^{2-} radicals were different than those observed in $\text{SrSO}_4/\text{CaSO}_4$ suggesting the role of matrix and dopant in stabilization of radicals. The thermal destruction of SO_4^- and hole trapping at UO_2^{2+} were found to be responsible for TSL peak observed at 411 K while 488 K peak was associated with destruction of SO_3^- .

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