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On the photophysics and speciation of actinide ion in MgAl₂O₄ spinel using photoluminescence spectroscopy and first principle calculation: A case study with uranium





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ABSTRACT

Actinide chemistry is very interesting not from scientific perspective but also from technological importance. Elucidating the valence state and coordinating environment of actinide ion like uranium in technologically important magnesium aluminate spinel (MAS) is important to fully understand its hazardous and other harmful effect in human as well as environment. Magnesium aluminate spinel doped with 1.0 mol % of Uranium ion has been synthesized using citric acid assisted gel-combustion route at 800 °C. The as prepared powder is characterised using X-ray diffraction (XRD), time resolved photoluminescence spectroscopy (TRPLS) and density functional theory (DFT) calculations. Uranium is an interesting element because it exhibits multiple oxidation state and each one of them is having characteristics fluorescence behavior. TRPLS is used to investigate the oxidation state and coordination behavior of uranium in MgAl₂O₄. Indeed in our earlier work on undoped and lanthanide ion doped MAS; it was oberved that in undoped sample itself defect induced emission could be seen in visible region which was probed using DFT. Here on doping uranium in MAS; complete energy of host is transferred to uranium ion which is explained using DFT. From excitation and emission spectroscopy it was observed that uranium stabilizes in +6 oxidation state in the form of UO_2^2+ ion. Based on luminescence lifetime and its comparison with the emission profile of uranyl fluoride crystal it was inferred that majority of uranium is occupying relatively asymmetric MgO₄ polyhedra and minority substitutes AlO₆. The site stability of the uranyl ion in MAS was also validated using DFT based first principle calculations. Time resolved emission shows the uranyl at Mg^{2+} site differs from the one at Al^{3+} site in terms of peak position and intensity.

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1. Introduction

MgAl₂O₄ belongs to spinel based inorganic compounds is an important material which finds application in diversified areas of science and technology. Some of the recent applications are in laser [1], light emitting diodes [2], catalysis [3], humidity sensor [4], luminescence host [5] etc. Other than this MgAl₂O₄ is proposed candidate for minor actinide transmutation; because of its favorable high temperature properties and high radiation stability [6]. It has been used extensively as a host for lanthanide luminescence like Ce^{3+} [7], Eu³⁺ [8], Tb³⁺ [9], Dy³⁺ [10], Gd³⁺ [11], Yb³⁺ [5] etc.

But actinides as dopant in MgAl₂O₄ ion have never been explored.

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.

Actinide chemistry recently has been gained new interest because of stabilization of various unusual oxidation states, unique magnetic properties and chemical reactivity. They are also very important for various applications such as in radiation shielding and ceramics, as ballasts in ships and airplanes and as a heat and fuel source in space exploration and in terrestrial nuclear power production [12]. Among all the actinides most of the research is focused on uranium and UO_2^{2+} ion in particular because it is the most dominant form of natural and spent uranium. The fact that U

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(+3), U (+4), U (+5) and U (+6) are all luminescence active ion and stabilizes under different conditions; time resolved photoluminescence (TRPL) is used extensively in uranium speciation in doped solid. In most of the cases U (+3), U (+4), U (+5) stabilizes in single crystal whereas U (+6) is most likely to get stabilized in solid powder. Some of the recent results from our laboratory suggested similar trends e.g. Uranium stabilizes as UO_2^{2+} in Sr₂SiO₄, Sr₂P₂O₇, ThO₂ [13–15] whereas as octahedral uranate UO_6^{6-} in SrZrO₃, SrB₄O₇ [16,17] etc. In some of the matrix uranium simultaneously stabilizes as U(IV) and U(VI) such as Gd₂Zr₂O₇ [18].

The luminescence properties of uranyl ion is quite remarkable; $UO_2^{2^+}$ gives bright green, vibrationally resolved ligand to-metal charge transfer (LMCT) emission in solution as well as in solid state [19]. Such fascinating uranyl luminescence has been explored for various applications such as photocatalysis [20], bio-remediation [21], chemosensor [22], internal actinometers in bio-logical chemistry [12].

Consider the fact that this $MgAl_2O_4$ is one of the probable candidates to be used for transmutation of actinide; speciation study of uranium ion in this particular matrix holds high significance for nuclear scientist. We have doped 1.0 mol % of uranium ion in combustion synthesized $MgAl_2O_4$ and tried to probe its local site occupancy, valence state and coordination geometry behavior using TRPL spectroscopy. We have used first principle DFT calculations to corroborate our luminescence data on local site occupancy and MAS to uranium energy transfer process.

Such combined experimental and theoretical approach to probe the local structure of actinide ion like uranium in MAS as well as MAS to UO_2^{2+} energy transfer dynamics has never been studied in actinide doped spinel material.

2. Experimental

2.1. Synthesis

MgAl₂O₄: U has been synthesized using gel-combustion method employing citric acid as combustion fuel. The raw materials used in this synthesis are citric acid ($C_6H_8O_7 \cdot H_2O$) (99.7%, AR grade), Magnesium Carbonate [MgCO₃] (99%, AR grade), Aluminium nitrate [Al (NO₃)₃·9H₂O] (98%, AR grade) and U₃O₈ (Spectroscopic Grade, 99.999%). At first Magnesium carbonate and uranium oxide was converted into their respective nitrate form by dissolving in appropriate amount of dilute nitric acid (4 M).

Secondly, magnesium and aluminium nitrates were dissolved in minimum amount of double distilled water and then were mixed with uranium nitrate solution. Citric acid was subsequently added to the resulting solution mixture. The molar ratio of the metal nitrates to citric acid was controlled at 1.0.

The entire mixing process was done at room temperature under vigorous stirring at magnetic stirrer and kept as such for 1 h. The solution mixture was then heated at 80 °C with continuous stirring for 5 h, until a highly viscous gel is formed. The gel was heated at under infra red lamp for 10–12 h after which a brown ash-like voluminous product was formed. The ash like mass was then grounded and kept for calcining at 800° C in a muffle furnace under air atmosphere for 12 h, after which a fine white powder was obtained.

2.2. Instrumental technique

Powders XRD patterns of the undoped and doped compounds were recorded using RIGAKU Miniflex-600 diffractometer operating in the Bragg-Brentano focusing geometry using Cu-K α radiation ($\lambda = 1.5406$ Å) as an X-ray source with operating condition of 40 kV voltage and 30 mA current. The XRD patterns were taken in the 2θ range of 10° — 80° with scan rate of 1° /minute. Time resolved PL measurements were carried out on an Edinburgh CD-920 unit equipped with M300 grating monochromators (placed on either side of sample). The data acquisition and analysis were done by F900 software. A 150 W Xenon flash lamp having variable frequency range of 10–100 Hz was used as the excitation source. Multiple emission and excitation scans (at least five) were taken to minimize the fluctuations in peak intensity and maximize signal-noise ratio. Approximately 25 mg of powder sample mixed with few drops of 4% collodion solution in the form of slurry was pasted over a glass plate. This was dried under ambient temperature and used for further studies.

2.3. Theoretical methodology

The normal phase of face-centered cubic MgAl₂O₄ spinel is studied using the Vienna ab initio simulation package (VASP) [23,24], which solve the Kohn–Sham equation within the framework of density functional theory (DFT). The calculations have been performed using the generalized gradient approximation (GGA) and the exchange and correlation energy per electron have been described by the Perdew-Burke-Ernzerhof (PBE) parameterization [25]. The ion-electrons interaction are described by the projector augmented-wave (PAW) method [26] using Mg (3s - 2 valence electrons), Al (3s, 3p - 3 valence electrons), O (2s, 2p - 6 valence electrons) and U (6d, 5f - 14 valence electrons) as implemented in the VASP potential database. For cubic spinel unit-cell as well as defect structures (comprises of oxygen vacancy (neutral and charged)) optimization was carried out with respect to E_{cut} and kpoint meshes to ensure convergence of total energy to within a precision 0.1 meV/atom. The Brillouin zone integration was performed on a Monkhorst-Pack [27] k-space sampling of $13 \times 13 \times 13$ in reciprocal space and a cutoff energy (Ecut) of 500 eV was used for the plane wave basis set. The total energy of normal cubic spinel unit-cell as well as structures comprises of oxygen vacancy (neutral and charged) were optimized with respect to volume (or lattice parameter) and atomic positions. Conjugate gradient algorithm was used for the unit-cell relaxations until the residual forces and stress in the equilibrium geometry were of the order of 0.005 eV/Å and 0.01 GPa, respectively. The final calculation of total electronic energy and density of states (DOS) were performed using the tetrahedron method with Blöchl corrections [28].

The Hubbard U correction was introduced for the uranium 5f electrons using the method proposed by Dudarev et al. [29], in which the *U* parameter (reflecting the strength of on-site Coulomb interaction) and *J* parameter (adjusting the strength of exchange interaction) are combined into a single parameter $U_{eff} = U$ -*J* to take care of the Coulomb repulsion between the localized f-electrons of the uranium atom. The values we employed were $U_{eff}(U) = 4.0$ eV as proposed by Xiao-Dong Wen et al. [30].

3. Results and discussion

3.1. XRD study

Fig. 1 shows the XRD patterns of as-prepared sample1.0 mol % U doped MgAl₂O₄. XRD patterns of samples are in close agreement with reported cubic pattern of MgAl₂O₄ with JCPDS No. 77-0435. The XRD patterns do not show any signature of impure diffraction peaks such as MgO, Al₂O₃ or U₃O₈ phase which is an indication of homogeneous solid solution of MgAl₂O₄ and U, which further confirms the occupancy of uranium ions in the lattice sites at either Mg^{2+} or Al³⁺ in MgAl₂O₄. It can also be seen from the XRD pattern that all peaks are sharp and well defined, indicating a high degree of crystallization in MgAl₂O₄:U sample. We have synthesized the



Fig. 1. Powder X-ray diffraction pattern of MgAl₂O₄: U.

pure phase at 800 °C and on comparison to reported literature our samples mostly stabilizes in normal spinel form with octahedral Al^{3+} and tetrahedral Mg^{2+} sites [31].

3.2. Luminescence study

Fig. 2 shows the emission spectrum of MAS undoped sample under 230 nm excitation. The emission can be seen in the visible bluish green region which was attributed to presence of shallow and deep defect in band gap of materials. Since the excitation wavelength used in this case is less than the band gap of MAS; direct band-to- band transition is not possible. There must be some defect states (cation or oxygen vacancies) which is aiding the holerecombination process. The origin and role of various defects is explained in our earlier work [32,33].

Fig. 3 depicts the excitation spectrum of MgAl₂O₄:U under emission at 501 nm. There are two main features one is a broad band at around 260 nm and there are cluster of peaks at around 422 nm. Broad peak at 260 nm has been attributed to a U–O charge transfer transition corresponding to the presence of U ions at the Mg²⁺ or Al³⁺ sites. The peak at 422 nm is typical of uranium in the form of uranyl ion. It is reported [34] that the absorption band at



Fig. 2. Emission spectrum of $MgAl_2O_4$ under excitation of 230 nm. *Reproduced from Ref: Gupta* et al. *RSC Advances, 2016, 6, 42923. DOI:* 10.1039/c6ra03369e with permission from the Royal Society of Chemistry.



Fig. 3. Excitation spectrum of MgAl₂O₄:U (λ_{em}-501 nm).

420 nm is typical of ligand-to-metal charge transfer (LMCT) electronic transition of uranyl (VI) salts consisting vibrational fine structure of which maximum of twelve transitions can be resolved. Fig. 4(a) shows the emission spectrum of MgAl2O4:U under



Fig. 4. Emission spectra of MgAl_2O_4:U in the excitation range (a) 230–300 and (b) 300-400.

excitation range from 230 to 300 nm. The spectral feature remains same as a function of excitation wavelength but they do differ in terms of intensity; 250 nm excited sample gives the maximum emission output. The fluorescence spectrum has six characteristic bands at 460, 480, 500, 520, 546 and 572 nm. The four main peaks (460, 480, 500, and 520 nm) have a full width at half maxima (FWMH) of around 20 nm (Fig. 4(a).). Complete disappearance of defect induced host emission of MAS in emission spectrum of uranium doped MAS is an indicative of the fact that complete energy transfer takes place at 1.0 mol % of uranium ion concentration. This we have tried to explain using DFT calculation in section 3.3.

Such vibronic progression with constant spacing is specific signature of uranium in +6 oxidation state in the form of UO_2^{2+} [13]. Such uniformly distributed vibrational progression arises from strong interaction of the ground state Raman active O=U=O symmetric stretching mode with the ${}^{3}\Pi_{u}$ electronic triplet excited state (generally observed between 780 and 900 cm⁻¹). These characteristic emission peaks of MgAl₂O₄:U (Fig. 4(a)) is due to LMCT involving electronic transition from bonding oxygen orbital (σ_u, σ_g , $\pi_{\rm u}$ and $\pi_{\rm g}$) to a non-bonding uranium 5f_{δ} and 5f_{ϕ} orbital [12]. U–O in uranyl ion (UO₂) has partial triple bond character and relatively shorter bond length compared to single U–O bond in uranate ion (UO₆). The position of first vibrational band (v_{0-0}) is most confirmatory signature in deciding the number of oxygen around uranium and bond order of U–O. And it is termed as zero phonon band (ZPB). ZPB for UO_2^{2+} can vary from 440 to 520 nm and the fact in our spectrum it is observed at 460 and the subsequent vibrational progression can be seen at room temperature is an indication of the fact U (+6) stabilizes as UO_2^{2+} .

Fig. 4(b) shows the emission spectra for the uranium incorporated MgAl₂O₄ samples as a function of excitation wavelength from 300 to 400 nm. It is seen from the figure that as the excitation wavelength increases and reached the limit of 330 nm the fine uranyl structures vanishes and a broad band was observed centered at around 525 nm which is the signature of uranate ion in octahedral coordination (UO_6^{6-}).

3.3. Efficient energy transfer from defect related emission of host to uranyl ion- A DFT study

In order to study the change in electronic structure of MgAl₂O₄ normal spinel with the oxygen defects and U atom doped in Mg site, the total and angular momentum decomposed density of states (DOS) is calculated and plotted in Fig. 5. Fig. 5(a) shows DFT calculated DOS of pure MgAl₂O₄ (normal spinel) which shows lower part of the valence band (VB) is mainly composed of s-states of Al, Mg and upper part of VB comprises of p-states of Al, Mg and O. On the other hand, lower part of conduction band (CB) is contributed by s and p states of Mg majorly as well as s and p states of Al. The GGA-PBE calculated electronic band-gap is 6.0 eV, which is lower compared to experimentally reported value of 7.8 eV (direct band-gap at Γ point) measured from optical reflectivity experiment [35]. Underestimation of band-gap is a well known limitation of the GGA [36–39]. In this study we focus on the change of the band-gap due to presence of O vacancy (neutral and charged), so it is expected to cancel the GGA-PBE calculated band-gap error during comparison.

In order to understand the change in electronic structure of normal spinel MgAl₂O₄ due to the oxygen vacancy, we calculated DOS of V_0^0 (neutral O vacancy), V_0^{+1} (O vacancy of charge +1) and V_0^{+1} (O vacancy of charge +2) and those results has already been elaborated in our previous study [32]. In the defective unit-cell, U atom is doped in Mg site and the change in the electronic DOS is shown in Fig. 5(b), (c) and (d). Uranium doping was done preferentially on Mg site as it is energetically favorable compared to

doping in Al site of normal spinel MgAl₂O₄.

Fig. 5(b) shows the total and angular momentum decomposed DOS in the presence of neutral O vacancy and U atom doped in Mg site. The spin-up and spin-down components are shown separately in upper and lower panels, respectively. Overall nature of the VB remains unchanged and an impurity band that appears 2.3 eV ahead of VB maximum in the band-gap is mainly due to neutral oxygen defect comprises of Mg-s and O-p states [32]. Moreover, an additional impurity band appears just below the CB, mainly contributed by U-f states in the spin-up component. Fermi level is moved towards the CB compared to normal spinel structure.

Fig. 5(c) shows the total and angular momentum decomposed DOS in the presence of O vacancy with charge +1 (V₀⁺¹). Overall nature of the VB remains unchanged but two impurity bands appear in the band-gap below the Fermi level. The impurity states are present 2.5 eV and 5.1 eV above the VB maximum. Impurity levels that are present near the VB maximum arises due to +1 charged oxygen vacancy which is composed of s-states of Mg and p-states of O [32]. U f-states has a significant contribution in the spin-up component in that impurity band. Impurity band present just at the Fermi level is solely contributed by the U f-states.

Fig. 5(d) shows the total and angular momentum decomposed DOS in the presence of O vacancy with charge +2 (V_0^{+2}). Overall nature of the VB remains unchanged but three impurity bands appear above VB maximum and below the Fermi energy. Impurity bands near VB are composed of f-states of U and impurity states just below the Fermi-level are composed of s-states of Mg and p-states of oxygen which arises due to +2 charged oxygen defect. These impurity states are filled with electrons as it is situated just below the Fermi energy. Impurities bands appear just below the CB minimum are solely composed of f-states of U.

U d and f-states contribute strongly in the lower part of CB as well as in the defect states generated due to oxygen vacancies. In our previous study [32] we have shown that photo-luminescence properties of the MgAl₂O₄ are dominantly governed by the defect states coming from the presence of oxygen vacancies (neutral and charged). As a result photon energy transfer from host MgAl₂O₄ to dopant U is easy and preferable.

3.4. Local site occupancy of uranium in MgAl₂O₄ spinel

In order to compare the emission profile of uranyl ion in a magnesium aluminate spinel and that of pure uranyl ion compound we have synthesized uranyl fluoride and recorded its fluorescence spectrum. Fig. 6 shows the comparative emission spectra of uranyl fluoride crystal systems and that of MgAl₂O₄: U. The emission spectrum of MgAl₂O₄: U exhibit broad spectral features compared to uranyl fluoride crystal; which is typical of uranyl ion in disordered chemical surrounding. Secondly, the emission bands in MgAl₂O₄: U are blue shifted w.r.t to peak position of uranyl fluoride which also indicates a distorted chemical environment for the uranyl ion in magnesium aluminate compared to pure uranyl compound. This indicates that majority of UO₂²⁺ occupies relatively asymmetric Mg²⁺ site (tetrahedral) in magnesium aluminate.

To get better insight into local structure and site of uranyl ion in magnesium aluminate, we have conducted luminescence life time measurements. The decay curves corresponding to the uranyl ions in magnesium aluminate spinel are depicted in Fig. 7 under excitation wavelengths of 250 nm monitoring emission at 501 nm.

The PL decay curve was fitted using bi-exponential model using equation:



Fig. 5. Total and angular momentum decomposed density of states (DOS) of pure normal spinel (a), U doped neutral oxygen vacancy (V_{0}^{0}) (b), U doped oxygen vacancy with charge +1 (V_{1}^{+1}) (c) and U doped oxygen vacancy with charge +2 (V_{2}^{+0}) in MgAl₂O₄. Vertical lines at zero energy represent Fermi level.



Fig. 6. Emission spectra of $MgAl_2O_4{:}U$ and uranyl fluoride crystals under identical conditions.



Where I(t) is intensity, τ_1 and τ_2 are emission decay times, and A_1 and A_2 are their relative weightage. The decay curve shows two different lifetime value 15 and 119 μ s with magnitudes 22 and 78%



Fig. 7. Luminescence decay profile of Uranyl ion in MgAl_2O_4 under $\lambda_{ex}\text{-}250$ nm and $\lambda_{em}\text{-}501$ nm.

respectively. Bi-exponential decay indicates different chemical environment of uranyl ion in MgAl₂O₄.

Assuming a given phonon energy (same host for the lanthanide/ actinide ions), a relatively longer luminescence life time should be attributed to a relatively more symmetric site, as the f-f transition becomes more forbidden, whereas a shorter life time is often associated with an asymmetric site due to relaxation in the f-f selection rules but we are getting reverse trend due to probable role of charge compensating defects. Species T₁ (15 μ s) which is the minor one arises because of uranyl ions occupying 6-coordinated Al³⁺ site with inversion symmetry whereas major species T₂ (119 μ s) can be ascribed to uranyl ions occupying 4-coordinated Mg²⁺ without inversion symmetry. These results are further substantiated by DFT measurements.

3.5. Corroborating the PL kinetics results using DFT calculations

MgAl₂O₄ normal spinel has a face-centered-cubic structure having space group Fd3m (O^h₇) where Al and Mg ions are in octahedral (local point group symmetry D_{3d}) and tetrahedral coordination (local point group symmetry T_d). Crystal structure of normal spinel is represented by lattice constant (a_0) and oxygen parameter (u). In the normal spinel, our DFT calculated a_0 , u, Mg–O and Al–O bond lengths are 8.16 Å, 0.263, 1.96 and 1.94 Å, respectively, which are in good agreement with previous experimental results [32].

In order to understand structural stability under U doping in Mg and Al site, selectively, in normal phase of MgAl₂O₄, the cohesive energies (E₀) and equilibrium volumes (V₀) were calculated after doping one U atom in Mg and Al site separately in the unit-cell of MgAl₂O₄. After doping, structures were fully relaxed as described in section Computational details. In our calculations we considered 1/ 56 (1.786%) doping level of U in normal phase of MgAl₂O₄ and results are shown in Table 1. Our DFT calculated cohesive energy difference of U doped supercells (in Mg and Al positions separately) is 1.524 eV for 56 atom unit-cell. U doping in Mg position is energetically more favorable than doping in Al position. Moreover, U doping in Mg and Al position increases the unit-cell volume by 18.44 Å³ and 22.36 Å³, respectively, compared to equilibrium volume of pure MgAl₂O₄ (543.34 Å³).

3.6. Time resolved emission spectroscopic analysis

To get information about emission characteristics of T_1 and T_2 , a time resolved emission spectroscopic (TRES) measurement was done on MgAl₂O₄:U. On applying suitable delay and selecting appropriate gate width, one can get emission spectral information for T_1 (15 μ s) and T_2 (119 μ s) (a detail related to TRES data slicing is provided as Supplementary information as I–1). The emission profile obtained for shorter and longer lived species is shown in Fig. 8. It can be seen from the spectra that the emission peaks corresponding to the slow decaying species are blue shifted by 3–5 nm and also both the species differ in their emission output. This observation clear confirmed the presence of the uranyl ion at two different chemical environments in MgAl₂O₄.

4. Conclusion

1.0 mol % Uranium doped MgAl₂O₄ is synthesized using gelcombustion method employing citric acid as fuel. The phase

Table 1

DFT calculated energies and super cell volume of site selective U ion doping in normal phase of MgAl₂O₄. $\Delta E_{cohesive}$ represents cohesive energy difference in site selective doping with respect to most energetically stable configuration.

Position of Eu doping	$\Delta E_{cohesive}$ in eV	Super-cell volume in Å ³
Mg position	0	561.78
Al position	1.524	565.70

 $\begin{array}{c} 2x10^{4} \\ 1x10^{4} \\ 0 \\ 400 \\ 450 \\ 500 \\ 550 \\ 600 \\ 650 \\ \end{array}$

Fig. 8. Time resolved emission spectra of short and longer lived uranyl ion in MAS.

purity of the material is confirmed using XRD. Speciation and local site occupancy of uranium in MgAl₂O₄ is studied using TRPLS. It was oberved that on irradiating MgAl₂O₄ with ultra violet light it gives visible emission which was attributed to presence of defect states within the band gap of MAS. The fact that there is no broad signature of defect induced host luminescence in the emission profile of Uranium doped MgAl₂O₄ is indicative of the fact that complete host to dopant energy transfer has taken place. Based on DFT based density of state calculation for Uranium doped MAS; it was oberved that Uranium d and f-states contribute strongly in the lower part of CB as well as in the defect states generated due to oxygen vacancies. In our previous study [32] it was seen that PL in undoped MAS is due to the defect states coming from the presence of oxygen vacancies (neutral and charged). As a result photon energy transfer from host MgAl₂O₄ to dopant U is highly favorable. Moreover the emission profile shows intense green emission consisting of equidistant vibronic progression 460, 480, 500, 520, 546 and 572 nm which are typical of UO_2^{2+} . The excitation spectrum shows a 422 nm band which is another fingerprint for absorption band of uranyl ion. The emission peaks are blue shifted and broad compared to that of pure uranyl fluoride crystal which is indicative of disordered geometry around uranyl ion in MgAl₂O₄. This was further confirmed from the luminescence lifetime data. Biexponential decay is observed which indicates two different chemical environments for uranyl ion in MgAl₂O₄. Species T₁ (15 us) which is the minor one arises because of UO_2^{2+} ions occupying 6-coordinated Al³⁺ site with inversion symmetry whereas major species T_2 (119 µs) can be ascribed to UO_2^{2+} ions occupying 4coordinated Mg²⁺ without inversion symmetry. DFT calculated energies and super cell volume of site selective U ion doping in normal phase of MgAl₂O₄ also showed uranium doping in Mg²⁺ position is energetically more favorable than doping at Al³⁺ site. Time resolved emission spectra obtained after suitable delay time shows the emission characteristics of uranyl at Mg^{2+} site differs slightly from the one at Al³⁺ site in terms of peak position and intensity.

This study is not important only from nuclear industry perspective but it will always open a new gate way from researcher working in the field of actinide spectroscopy.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jallcom.2016.10.209.

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