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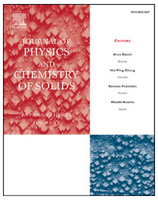

Trap level spectroscopic investigations of U: $ZnAl_2O_4$: Role of defect centres in the TSL process

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ABSTRACT

In order to evaluate the trap level spectroscopic properties of Uranium in $ZnAl_2O_4$ spinel host, undoped and Uranium doped $ZnAl_2O_4$ samples were synthesized. From photoluminescence (PL) data it was confirmed that uranium gets stabilized in the system as UO_6^{6-} (octahedral uranate). Electron spin resonance (ESR) studies for the gamma irradiated sample suggested the formation of O^{2-}, F^+ and V centres. From the TSL (thermally stimulated luminescence) data, the trap parameters such as frequency factor and activation energy etc. were evaluated. From ESR-TSL correlation it was confirmed that the destruction of O^{2-} ion coincides with TSL glow peak appeared at 332 K.

1. Introduction

Majority of the actinide ions exhibit vivid spectroscopic properties due to the unique electronic configuration. These properties play a very important role in the understanding of their electronic structure and nature of chemical bonding with various ligands. Photoluminescence (PL) is a phenomena where radiative emission of energy from any species (molecule, atom or ion) occurs upon excitation by photons. Several metal ions, especially lanthanides are known to show PL emission. Among the actinide group elements, Uranium is known to give efficient PL when suitably excited with photons. One may find plenty of reports on the PL properties of uranium in different oxidation states (VI, V, IV, III) [1,2]. However, among them, the hexavalent uranium species, uranyl ion (UO_2^{2+}) is the most commonly encountered one. When excited by wavelengths in the ultraviolet (UV) region, this uranyl species is known exhibit characteristic emission in the 450–600 nm region. In addition to this uranyl species, other hexavalent species of uranium such as UO_6^{6-} and UO_4^{2-} (octahedral and tetrahedral uranate groups respectively) are also reported to show efficient PL when excited suitably [3]. The electronic spectra of actinide ions are usually studied after stabilizing them in crystalline host matrices, which make the Laporte for biddenness (of the transitions) less rigorous.

Zinc aluminate ($ZnAl_2O_4$ = ZA) is a well known spinel and a wide-band-gap (~3.9 eV) material that fits into an appropriate host category which can be easily used for dopant based phosphor materials [4,5]. Though synthesis dependent, it is often believed that, ZA stabilises itself in a normal spinel structure having lower cationic disorders. Thus, it has been explored extensively in various industries owing to its excellent electrical and thermo-mechanical properties. ZA has been previously used in laser and ceramic industries, photo electronic devices, display technologies, chemical sensing applications, catalytic applications and dosimetric materials etc [6–8]. Further, there are many reports suggesting the use of ZA as a potential luminescence host matrix for different lanthanide and transition metal ions. Recently, we had investigated the energy transfer mechansim in ZA codoped with Eu and U [9].

Activation energy (E_a) and frequency factor (s) for any radical species (collectively referred to as trap parameters) play a major role in the process of TSL (thermally stimulated luminescence). These trap level spectroscopic properties also decide the usability of any sample as a (TSL) dosimetric material. Moreover, these properties are essential for a better understanding of the basic TSL mechanism (spectroscopic process).

Although one may find plethora of literature reports on the PL properties of Uranium, the TSL process of uranium incorporated systems are in scarce. Our group has earlier reported the trap parameters of this actinide ion (uranium) in different hosts [10–12]. The present paper focuses on understanding the trap parameters in ZA host using ESR, TSL and PL techniques. TSL can give an idea regarding the trap parameters and order of kinetic of the glow peaks observed in the gamma-irradiated samples. From the data, it is also possible to have an idea about formation of defect centres in the system. PL spectroscopic technique helps to identify the species (of uranium) responsible for the luminescence. ESR (electron spin resonance) technique helps to identify the chemical nature

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of the trap sites (radical species) responsible for the observed glow peak. By correlating the results obtained from PL and ESR, a complete mechansim for any TSL process can be ascertained.

2. Experimental

2.1. Synthesis of samples

Polycrystalline samples of undoped ZA and uranium doped ZA (1 mol %) were synthesized via a sol-gel method at 1173 K. Analytical grade (Fluka) Zinc Nitrate [$Zn(NO_3)_2 \cdot 6H_2O$], Aluminum Nitrate [$Al(NO_3)_2 \cdot 9H_2O$], Uranyl Nitrate [$UO_2(NO_3)_2$] and Citric Acid [$C_6H_8O_7 \cdot H_2O$] were used as the starting materials. Stoichiometric quantities of the metal nitrates were mixed so as to fix 1 mol% doping. Further, stoichiometric amount of Citric Acid was added to the mixture and the solution was continuously stirred on a hot plate at 343 K to form a highly viscous gel. This was subsequently calcined at temperatures between 973 and 1173 K to obtain fine white powder of the final compound. The final calcination was carried out in a muffle furnace, which was maintained at 1173 K. The sample was calcined for 4 h at each step of heating treatment. Undoped sample was prepared in a similar manner.

2.2. Instrumentation

The phase purity of the synthesized phosphors was confirmed using a STOE X Ray Diffraction (XRD) unit equipped with Ni filter, scintillation counter and graphite monochromator. The diffraction patterns were obtained using monochromatic Cu K_α radiation with $\lambda = 1.5418$ Å. The PL measurements of excitation and emission spectra were carried out using an Edinburgh F-900 Fluorescence spectrometer. TSL glow curves in the temperature range 300–550 K with a various heating rates and emission spectra at constant temperature were recorded using home-built unit. ESR spectra were recorded at room temperature using a Bruker EMX series spectrometer (EMM1843) operated at X-band frequency. The ‘g'values were calibrated relative to a 2,2 diphenyl-1 picryl hydrazil (DPPH) standard. $A^{60}Co$ source having dose rate of 1 kGy/h was used for gamma irradiation studies.

3. Results and discussion

3.1. XRD investigations

XRD patterns of un-doped and uranium doped ZA along with the standard pattern for cubic ZA spinel are shown in Fig. 1. All the observed diffraction peaks could be indexed on to spinel ZA phase with cell parameter ‘a’ = 8.059 °A (ICCD file no. 5-669).

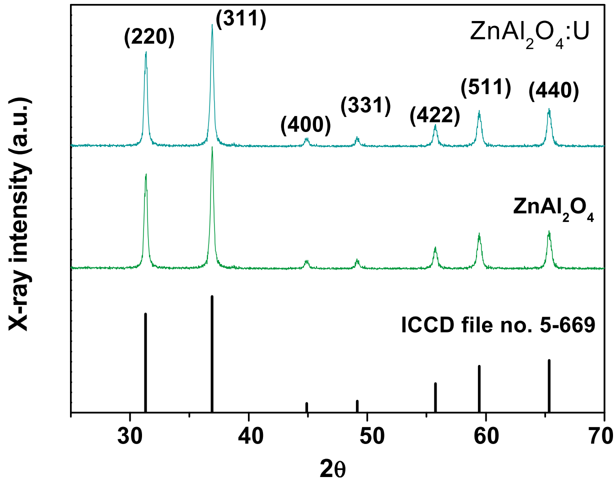

Fig. 1. XRD patterns of blank $ZnAl_2O_4$ and U doped (1 mol%) $ZnAl_2O_4$.

In AB_2O_4 spinels, ’A’ is generally a divalent (2+) cation whereas B is trivalent (3+) cation. Out of the 64 tetrahedral interstices, 8 are occupied by A^{2+} cations. On the other hand, 32 of the octahedral interstices, 16 are occupied by B^{3+} cations. The occupancy of the octahedral/tetrahedral sites are prescribed by factors, such as, ionic size, cationic charge, electron distribution and state. In a normal spinel, such as ZA, the 3+ ions of ’Al’ substitute at the octahedral sites while the 2+ ions of ’Zn’ occupy the tetrahedral sites. While in an inverse spinel, the divalent and trivalent ions are not only exchanged but also there is definite chance of mixed substitution by different amounts of A^{2+} and B^{3+} on the octahedral. However, the tetrahedral sites are only substituted by the B^{3+} cations.

In the present case it can be observed that the XRD patterns of the undoped and uranium doped ZA are identical. There are few probable reasons for this result. One may be attributed to a well dispersed uranium species in the ZA matrix so that it represents a homogenous system throughout. Another possibility is the small amount of the (1 mol%) dopant ion that is unable to create any major changes in the electronic structure factor. We assume that it is the later one here that causes the similarities in the two XRD patterns.

3.2. PL investigations

To ascertain the site position of the dopant Uranium ions, PL studies were performed.

Fig. 2 (a) and (b) show the excitation and emission spectra for the undoped and uranium doped ZA with $\lambda_{ex} = 248$ nm and $\lambda_{em} = 519$ nm respectively. It can be seen that the undoped sample showed weak emission and excitation characterstics with no definite peak positions. However, on doping with uranium both the emission and excitation spectra showed the characterstics of uranium ion. The excitation spectrum is represented by the presence of a number of peaks at 230, 248, 261, 271, 285, and 295 nm. Similarly, the emission spectrum also showed the presence of four relatively broad bands centered at 505, 519, 544 and 576 nm.

A glance at the literature reports suggests that the uranyl ion (UO_2^{2+}) is the most commonly encountered luminescent species of hexavalent uranium. This is characterized by the presence of a five-line structure in the emission spectrum with the zero-phonon (zp) line appearing in the range 480–520 nm [13,14]. However, as stated earlier, the uranyl moiety is not the only luminescent species of uranium. Tetrahedral (T_d) and octahedral (O_h) uranate groups (UO_4^{2-}, UO_6^{6-} and U^{6+}) are also known to produce intense PL. Both UO_2^{2+} and octahedral UO_6^{6-} give emission in the green region from Uranium-activated phosphors, but uranyl emission can be distinguished from that of the latter based on its characteristic vibronic structure exhibiting set of equidistant lines. The characteristic emission of tetrahedral uranate (UO_4^{2-}) species was reported to be in the red region. Recently, Pote et al. have reported the uranate group in CaF_2:U phosphor [15]. The octahedral uranate (UO_6^{6-}) having structure less green emission has been reported in many systems such as SrB_4O_7, $SrZrO_3$, and SrO [16]. In the present case, the emission and excitation spectra resemble more that of the octahedral uranate $(UO_6)^{6-}$ species. Therefore, it was concluded that the observed broad green emission band without any prominent vibronic structure is due to uranate $(UO_6)^{6-}$ moeity. The origin of this emission is assigned to the parity forbidden charge transfer transition 5f—t_{1u} that is vibronically coupled by the ungerade vibrational modes of the UO_6^{6-} octahedron. To confirm this stabilization of the octahedral uranate in the matrix, PL decay time measurements were done on the ZA:U system.

Fig. 3 shows PL decay time measurements on the ZA:U system with 248 nm excitation and 519 nm emission wavelengths. The luminescence decay curve was recorded on 2000 μs scale. The exponential decay equation used for fitting is mathematically represented as given below.

$$I(t) = a_0 + \sum_{n=1}^{n} \left(a_n \exp \frac{-t}{\tau_n} \right)$$