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Luminescence of the uranyl-ion-doped elpasolite lattice

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Abstract

Distinct species U(III), U(IV), U(V) and U(VI) have been identified when U(VI) or U(IV) species are doped into the cubic elpasolite lattice. The band intensities, and derived vibrational frequencies, in the luminescence and absorption spectra of the uranyl ion situated in this lattice are compared with those of Cs₂UO₂Cl₄. In particular, the intensity enhancement of the B_{2g} → A_{1g}(D_{4h}) hypersensitive transition shows that the uranyl ion occupies a majority site of C_{2v} or lower symmetry.

1. Introduction

Denning and co-workers have provided a comprehensive model of the electronic structure of the uranyl ion, UO₂²⁺, from studies of high-symmetry solid-state compounds [1]. Although the luminescence spectra of this chromophore are well characterized for neat solids, there have been fewer studies of the luminescence of this ion diluted into transparent crystalline hosts [2–4]. We have previously investigated the spectral behaviour [5] and energy-transfer phenomena [6] of tri-positive lanthanide ions situated in cubic elpasolite crystals. The aim of the present study is to characterize the emission of the uranyl ion in this host lattice, as a prelude to energy-transfer studies with co-doped lanthanide ions. It was also envisaged that the perturbations upon the ion arising from charge inequality and vacancy size would present interesting spectral ramifications. As subsequently discussed in detail, the spectral intensities provide information concerning the uranyl site symmetry, and the derived vibrational frequencies enable changes in bond distances to be followed. The possible changes in oxidation state of hexavalent and tetravalent uranium upon doping into the tri-positive ion site were also felt to be worth investigation. Another di-positive cation, Eu²⁺, has been shown by room temperature EPR studies to occupy a trigonal-symmetry site in Cs₂NaYCl₆ and a cubic site in Cs₂NaEuCl₆ [7].

2. Experimental procedure

The investigations utilized one host, Cs₂NaYCl₆, which our absorption spectrum shows to be optically transparent below 50 000 cm⁻¹, and another, Cs₂NaGdCl₆, which is transparent up to the excited state ⁶P_{7/2} at 31 951 cm⁻¹ [8]. Both were prepared according to Morss method E

[9], and the uranyl ion was introduced as $\text{Cs}_2\text{UO}_2\text{Cl}_4$ into the hydrochloric acid solution. Uranium (IV) was doped into $\text{Cs}_2\text{NaYCl}_6$ by mixing with Cs_2UCl_6 in the solid phase, and then melting under vacuum in a sealed quartz tube; or by adding uranium (IV) hypophosphite solution to the hydrochloric acid solution prior to evaporation to dryness in Morss method E. Polycrystalline boules several cm long were grown in quartz tubes using a Bridgman furnace.

10 K absorption spectra were recorded at the resolution 2 cm^{-1} using a Biorad FTS-60A wide-range spectrometer equipped with a photomultiplier detector. The samples were housed in an Oxford Instruments closed-cycle cooler. 10 K Raman and argon-ion laser emission spectra of $\text{Cs}_2\text{NaGdCl}_6:\text{UO}_2\text{Cl}_4^{2-}$ were recorded using a Spex 1403DM system, at the resolution 2 cm^{-1} . Argon-ion laser-excited emission spectra of $\text{Cs}_2\text{NaYCl}_6:\text{UO}_2\text{Cl}_4^{2-}$ were recorded at the resolution $\approx 10\text{ cm}^{-1}$ at Hong Kong Baptist University. Excitation spectra were recorded at 300 K and 77 K by an SLM 4800C Spectrofluorometer using lower resolution, $\approx 40\text{ cm}^{-1}$. No uranyl emission was observed from these crystals, using 514.5 nm excitation at 80 K, because the uranyl-ion absorption bands lie to higher energy, but a rising background occurred which peaked near $17\,200\text{ cm}^{-1}$. Under 496.5 nm excitation at 20 K (which is only weakly absorbed by the uranyl ion), emission was observed similar to that under 476.5 nm excitation, but it was much weaker and broader. Superimposed upon the high-energy region of the spectrum ($20\,100\text{--}18\,100\text{ cm}^{-1}$), in addition to Raman bands, were more intense bands from another luminescent centre. A further luminescent centre was identified under 326 nm ($30\,675\text{ cm}^{-1}$) xenon lamp excitation, not only in doped samples but also in crystals of the $\text{Cs}_2\text{NaYCl}_6$ host lattice. ICP-AES analysis of undoped $\text{Cs}_2\text{NaYCl}_6$ crystals (prepared from 99.99% or 99.999% Y_2O_3 , Strem Chemicals) showed the presence of many metals at up to ppm levels. For this reason (and another subsequently given in section 4.2, concerning the presence of several different oxidation states of uranium in the crystals with the result that uranyl concentrations are a nominal maximum), we did not pursue detailed investigations of the ultraviolet excitation spectra of the uranyl ion.

3. Types of guest-ion site

$\text{Cs}_2\text{UO}_2\text{Cl}_4$ crystallizes in the space group $C2/m$ with one formula unit in the Bravais cell [10]. The U–O and U–Cl bond distances are 177.4 pm and 267.1 pm respectively. The crystallographic site symmetry of the $\text{UO}_2\text{Cl}_4^{2-}$ moiety is C_{2h} , but optical spectroscopic studies can be interpreted under D_{4h} selection rules [11], or under D_{2h} selection rules if small splittings of bands are taken into account [12]. The $Fm\bar{3}m$ elpasolite lattice contains one formula unit of $\text{Cs}_2\text{NaLnCl}_6$ in the Bravais cell, with octahedrally coordinated Na^+ , and also Ln^{3+} situated at O_h point group symmetry sites, whilst both Cs^+ are situated at T_h sites. The NaCl_6 and LnCl_6 octahedra are joined at corners, with Na–Cl and Ln–Cl distances of approximately $269 \pm 1\text{ pm}$ for $\text{Ln} = \text{Y, Gd}$ [13], similar to the U–Cl distance in $\text{Cs}_2\text{UO}_2\text{Cl}_4$. The Cs^+ cations are surrounded by 12 Cl^- , with the closest distance being $\approx 380\text{ pm}$ which is almost the sum of the ionic radii; and are arranged in eightfold coordination about Ln^{3+} (Cs–Ln distance: $\approx 460\text{ pm}$).

It is interesting to explore the sites that could be occupied by $\text{UO}_2\text{Cl}_4^{2-}$ in the elpasolite lattice. It might be envisaged that at sufficiently high concentrations these anions would enter the host lattice in pairs, occupying adjacent Ln^{3+} and Na^+ sites with the result that charge compensation is then unnecessary. In this case, the dimer site symmetry is D_{2h} if the uranyl axes are parallel, and D_{2d} if orthogonal, but the uranyl site symmetry is C_{2v} . It is anticipated that the electronic spectra of the dimer would show certain vibrational fingerprints such as the bridging chloride mode, as well as the coupling of ν_2 modes in the D_{2h} case. Single-site occupation by $\text{UO}_2\text{Cl}_4^{2-}$ could occur at the Cs^+ site, with two different types of Cl^- vacancy,

but then the U–Cl distance would either be too large or too small. Single-Ln³⁺-site occupation could occur with a Na⁺ vacancy adjacent to uranyl oxygen (C_{4v} site) or equatorial chloride (C_{2v} site); with a Cs⁺ vacancy (C_s or C₁ sites); or with charge compensation by interstitial negative ions. The C_{4v} site is expected to give rise to a stronger uranyl bond than the C_{2v} site. Replacement of NaCl₂[−] by UO₂²⁺, with a neighbouring Ln³⁺ vacancy, may occur to produce C_{4v} or C_{2v} sites. The Na⁺ site is of virtually the same size as the Ln³⁺ site. Various other types of charge compensation, involving electrons or holes, are possible for the guest-ion sites discussed above.

Since, under the experimental conditions employed for synthesis, a large excess of Cl[−] was present, and Cs⁺ salts were employed, it is probable that the Ln³⁺ or Na⁺ sites, rather than the Cs⁺ sites, are occupied by U⁶⁺. For the more deliquescent Cs₂NaYCl₆ host, interstitial charge compensation by OH[−] may occur to a greater extent, in addition to compensation by Cl[−].

4. Results and discussion

4.1. Argon-ion laser-excited luminescence of elpasolites doped with uranium (VI)

The first excited state of the uranyl ion coordinated to four equatorial chloride ligands is located near 20 000 cm^{−1} and is degenerate, transforming as the E_g representation in the D_{4h} molecular point group of the UO₂Cl₄^{2−} anion [1]. The vibrational modes of the UO₂Cl₄^{2−} anion relevant to the subsequent discussion are described in table 1. Figure 1 shows the high-energy region of the 476.5 nm excited 20 K luminescence spectrum of 0.5 mol% UO₂Cl₄^{2−} doped into Cs₂NaGdCl₆. The two highest energy bands (at 236 cm^{−1} and 292 cm^{−1} to low energy of the excitation line) correspond to the ε_g and α_{1g}(O_h) modes in the Raman spectrum of the Cs₂NaGdCl₆ host. The intense zero-phonon line (ZPL) at 19 951 cm^{−1} corresponds to the E_g → A_{1g}(D_{4h}) uranyl-ion transition. Comparison of this energy with those of the ZPL for other chloride host lattices for the UO₂Cl₄^{2−} ion, Cs₂SnCl₆ and Cs₂UO₂Cl₄, shows that a higher-energy ZPL, and consequently higher energy of excitation of σ_u to δ_u [1], is associated with shorter U–O bond distance, as exemplified by the magnitudes of the symmetric stretching vibration energies, ν₁ν_s(OUO). A shoulder is observed at ≈10 cm^{−1} to the low-energy side of the origin, and is also resolved at low energy of most other bands. In C_{4v} symmetry, the electric dipole-allowed (ED-allowed) E → A₁ transition would not be split, whereas at the C_{2v}-symmetry site the components A₂ → A₁ and B₁ → A₁ would be magnetic dipole (MD) and ED allowed respectively.

Table 1. Vibrational data from the luminescence spectra of UO₂Cl₄^{2−} at 10–20 K. (ν_s, ν_{as}: symmetric, antisymmetric stretch; δ: bend.)

| Derived vibrational energies (cm ^{−1}) | Host lattice with UO ₂ Cl ₄ ^{2−} | | |
|--|---|---------------------------------------|-------------------------------------|
| | Cs ₂ UO ₂ Cl ₄ [2] | Cs ₂ SnCl ₆ [3] | Cs ₂ NaGdCl ₆ |
| ν ₁ ν _s (OUO) | 836 | 821 | 832 |
| ν ₂ ν _{as} (OUO) | 917 | 905 | 914 |
| ν ₃ δ(OUO) | 244 | 249 | 252 |
| ν ₄ ν _s (UCl) | 266 | 279 | — |
| ν ₆ ν _{as} (UCl) | 265 | 276 | 264 |
| ν ₁₀ δ(OUCl) | 115 | 114 | 92 |
| ν ₁₁ δ(OUCl) | 200 | 201 | 200 |

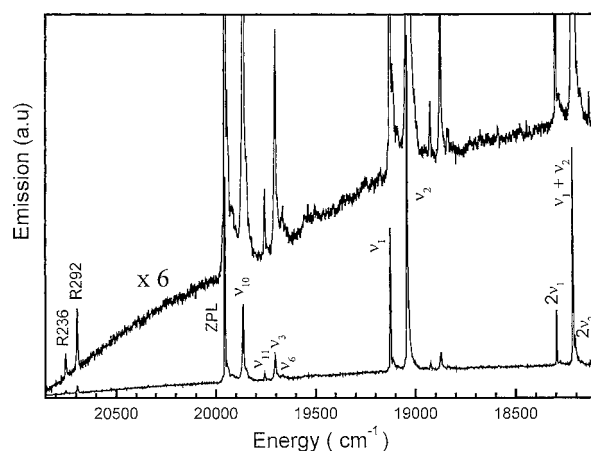


Figure 1. The 476.5 nm excited luminescence spectrum of $\text{Cs}_2\text{NaGdCl}_6$ doped with 0.5 mol% uranyl ions, between 20850 and 18100 cm^{-1} . (R: Raman; ZPL: zero-phonon line.)

In D_{4h} symmetry, the ZPL and progressions in the α_{1g} and ε_g modes thereupon, are enabled by the MD intensity mechanism. All other bands in the spectrum correspond to the excitation of single quanta of odd vibrational modes (and progressions thereupon), and are enabled by the ED vibronic mechanism. Both C_{4v} and C_{2v} noncentrosymmetric perturbations of the uranyl ion would introduce ED character into the pure electronic transition. A smaller intensity ratio of a particular vibronic origin to that of the ZPL indicates that the uranyl-ion pure electronic transition acquires greater ED character. This is found to be the case when comparing the relative intensity of the ν_{10} chloride bending mode compared with that of the ZPL: 1.2 for $\text{Cs}_2\text{UO}_2\text{Cl}_4$; 0.65 for $\text{Cs}_2\text{SnCl}_6:\text{UO}_2\text{Cl}_4^{2-}$; and 0.44 in the spectrum of $\text{Cs}_2\text{NaGdCl}_6:\text{UO}_2\text{Cl}_4^{2-}$. Similar observations apply to ν_2 and ν_3 . This noncentrosymmetric perturbation at the uranyl-ion site is strong enough to enable the appearance of progressions in the $\nu_2\nu_{\text{as}}$ (OUO) mode, with the first member based upon the electronic origin being observed as the lowest energy band in figure 1.

The vibrational energies derived from the luminescence spectrum are compared with those from the spectra of $\text{Cs}_2\text{UO}_2\text{Cl}_4$ and $\text{Cs}_2\text{SnCl}_6:\text{UO}_2\text{Cl}_4^{2-}$ in table 1, and the mode descriptions are included. The uranyl rocking mode appears more prominent in the spectrum of $\text{Cs}_2\text{NaGdCl}_6:\text{UO}_2\text{Cl}_4^{2-}$, acquiring ED character through the loss of the inversion centre. The spectrum is dominated by the uranyl modes ν_2 , ν_3 and ν_{11} , and the progressions in ν_1 upon these vibronic origins. The progressions in ν_{11} upon vibronic origins are much weaker, but nevertheless are stronger than those in ν_4 . The only modes with chloride-ion character which make a substantial intensity contribution to the luminescence spectrum are ν_6 and ν_{10} .

The energy of the chloride bending mode, ν_{10} , is lower than in $\text{Cs}_2\text{UO}_2\text{Cl}_4$ and $\text{Cs}_2\text{SnCl}_6:\text{UO}_2\text{Cl}_4^{2-}$ possibly due to guest–host coupling with the ν_4 (Cl–Gd–Cl) bending mode. Replacement of the SnCl_6^{2-} anion in Cs_2SnCl_6 (where the Sn–Cl distance is 243 pm) by $\text{UO}_2\text{Cl}_4^{2-}$ was shown to lead to axial elongation and equatorial compression of the guest ion [2]. In the case of $\text{Cs}_2\text{NaGdCl}_6:\text{UO}_2\text{Cl}_4^{2-}$, the host Gd–Cl bond distance is comparable with the U–Cl distance, so the U–Cl antisymmetric stretching mode energy is similar to that in $\text{Cs}_2\text{UO}_2\text{Cl}_4$. However, from table 1, the energies of uranyl stretching modes are only slightly lower than in $\text{Cs}_2\text{UO}_2\text{Cl}_4$.

Besides the appearance of ν_{10} hot-band structure based on both ZPL components, and a blurring of structure, two interesting changes are observed on warming to 80 K. First, the

ν_{11} hot band is observed at 172 cm^{-1} to the high-energy side of the ZPL. The energy of this mode in the E_g state is thus similar to that in $\text{Cs}_2\text{UO}_2\text{Cl}_4$. Second, a further zero-phonon line is observed at $20\,275 \pm 2\text{ cm}^{-1}$, with progressions in ν_s to lower energy with the same interval as $E_g \rightarrow A_{1g}(\text{D}_{4h})$. This prominent electronic origin corresponds to the hypersensitive $B_{2g} \rightarrow A_{1g}(\text{D}_{4h})$ transition, and taking into account the Boltzmann factor, its intensity is about 20 times greater than that of $E_g \rightarrow A_{1g}(\text{D}_{4h})$. The corresponding hypersensitive origin is not observed in the 80 K luminescence of $\text{Cs}_2\text{UO}_2\text{Cl}_4$, but is evident in low-symmetry salts of $\text{UO}_2\text{Cl}_4^{2-}$. The site symmetry of the uranyl ion must therefore be C_{2v} (or lower) because the ED intensity enhancement of this electric quadrupole-allowed (EQ-allowed) transition would not occur for a $B_2 \rightarrow A_1(\text{C}_{4v})$ transition.

The luminescence spectra of $\text{Cs}_2\text{NaYCl}_6:\text{UO}_2\text{Cl}_4^{2-}$ were generally not as well resolved as that discussed above, partly due to the presence of at least three major uranyl sites, with the ZPL between $19\,936$ and $19\,743\text{ cm}^{-1}$. The separations between the ZPLs of different sites was $>50\text{ cm}^{-1}$. The relative intensities of bands due to the different sites only showed minor changes when the uranyl concentration was decreased by the factor of 100. However, use of different Ar^+ -ion laser excitation lines produced changes in relative intensity that were >5 -fold.

4.2. Absorption spectrum of $\text{Cs}_2\text{NaYCl}_6$ doped with uranium species

Absorption spectra were recorded for samples of $\text{Cs}_2\text{NaYCl}_6$ doped with 0.05 and 0.5 mol% UO_2^{2+} , as well as with between 0.05 and 3 mol% UCl_6^{2-} . The results indicated the presence of several different uranium species in the crystals, so detailed spectral analyses were not carried out. However, some conclusions may be drawn from the spectra.

Figure 2 shows the region between $20\,200\text{ cm}^{-1}$ and $21\,600\text{ cm}^{-1}$ in the absorption spectrum of a crystal of $\text{Cs}_2\text{NaYCl}_6$ doped with 0.5 mol% UO_2^{2+} . The features marked ν exhibited variable relative intensity in different samples, with respect to the uranyl bands, and are not due to the uranyl ion. At higher dopant concentrations, many other features were observed in this region due to clusters of $\text{Cs}_2\text{UO}_2\text{Cl}_4$. The strong, sharp band at the lowest energy ($20\,278 \pm 2\text{ cm}^{-1}$) is assigned to the ZPL of the $A_1 \rightarrow B_2(\text{C}_{2v})$ transition of the uranyl ion [14]. Other bands are also assigned to the ZPL, or to ν_s progressions thereupon, with this excited-state stretching frequency being $6\text{--}8\text{ cm}^{-1}$ lower than in $\text{Cs}_2\text{UO}_2\text{Cl}_4$ [12].

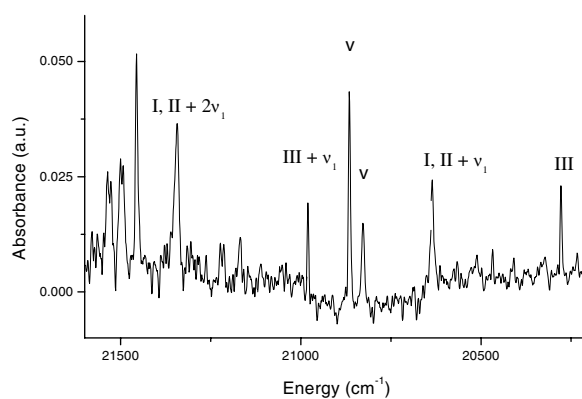


Figure 2. The 10 K absorption spectrum of $\text{Cs}_2\text{NaGdCl}_6$ doped with 0.5 mol% uranyl ions between $20\,200$ and $21\,600\text{ cm}^{-1}$. (Features marked ν exhibit variable relative intensity from one sample to another. The electronic origins are labelled in the notation of Denning [1].)

Some bands due to U^{4+} are clearly present at lower energy in the spectrum and their variable relative intensities from one sample to another indicate that several sites/species occur. Intense structure is observed at higher energy, between 23 500 and 27 500 cm^{-1} . These bands are not observed when U(IV) is diluted into Cs_2NaYCl_6 . Furthermore, they are not evident in the (low-resolution) excitation spectrum of the uranyl emission. The features clearly correspond to an ED-allowed transition ($f \rightarrow d$), and the progression frequency of $\approx 770\text{ cm}^{-1}$ is consistent with a uranium (V) chloro-oxo species.

Samples of Cs_2NaYCl_6 doped with U^{4+} were colourless or brown, and bands due to U^{4+} were observed in the absorption spectrum. However, after two years' storage at room temperature, the contents of the sealed quartz boules turned ink-blue. Comparison of the visible absorption spectrum with previous work [15] shows that the intense bands correspond to the vibrational progressions of $5f^3 \rightarrow 5f^26d^1$ electronic transitions of U^{3+} in UCl_6^{3-} . Some weak, sharp bands correspond to U^{4+} impurities.

5. Conclusions

Well-resolved low-temperature luminescence and absorption spectra of samples of $Cs_2NaGdCl_6:UO_2Cl_4^{2-}$ have been presented and discussed. In particular, the intensity enhancement of the $B_{2g} \rightarrow A_{1g}(D_{4h})$ hypersensitive transition shows that the uranyl ion occupies a majority site of C_{2v} or lower symmetry, at a concentration $\leq 0.5\%$. Several possible types of site have been discussed in section 3, and further experiments, such as high-resolution excitation spectroscopy, are required for more specific identification. Although the low-energy region of the spectrum for uranyl absorption in the Cs_2NaYCl_6 host is dominated by pure electronic ED transitions, the interpretation is consistent with that of higher-symmetry uranyl compounds [1]. In general, doping of U(VI) or U(IV) into the elpasolite lattice gives several uranium species, but U^{3+} is predominantly formed over a period of time when U(IV) is doped into Cs_2NaYCl_6 .

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