Emission Spectra and Luminescence Life Times of Uranium-Mica Type Compounds

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A series of uranium–mica type compounds $M(UO_2)_2(XO_4)_2 \cdot nH_2O$, where M=Ca, Sr, Ba, Mg, Na_2, K_2, and $(H_3O)_2$; X=P and As, as well as the doped samples of $Mg(UO_2)_2(PO_4)_2 \cdot nH_2O$: Mn(0.03 mol %) and $Zn(UO_2)_2(PO_4)_2 \cdot nH_2O$: Cu(0.1 mol %), have been prepared and measured for emission spectra under the UV-(365 nm) excitation and decay times. Some of these samples, *e.g.*, $(H_3O)_2(UO_2)_2(AsO_4)_2 \cdot nH_2O$, have been found to give weak shoulders and a separated band, in addition to the six bands so far reported for other uranyl(VI) compounds. Samples containing AsO_4^{3-} ions in place of PO_4^{3-} gave emission spectra, where the main bands shifted by approximately 100 cm^{-1} to lower energy also giving shorter life times. The decay times of the six emission bands of $Mg(UO_2)_2(PO_4)_2 \cdot nH_2O$ have been found to have the same value of 2.5×10^{-4} s.

Uranyl(VI) compounds exhibit a highly characteristic luminescence both in the solid state and in solution. The spectral properties of uranyl(VI) compounds have been studied in great detail, since Stokes gave the first systematic investigation on light-emission and absorption in the middle of the nineteenth century.[1-4] The theoretical basis, however, for understanding the spectroscopic properties of the UO_2 group has been established only in the last two or three decades and remain incomplete.[5,6] The luminescence, which is assigned to emission from the lowest excited $^3\Pi_u$ state displays considerable sub-structure probably due to vibrational effects. Bell and Biggers,[6] who gave possibly the most comprehensive analysis of Uranyl(VI) salts, resolved the six emission bands in the luminescence spectrum of uranyl(VI) perchlorate in water. Iimori and Iwase resolved the sixteen bands of the fluorescence spectrum of natural autunite, a hydrous phosphate of uranyl (VI) and calcium, by photo techniques.[7] No further description has, however, been published on the luminescence spectrum of this mineral. In the present paper, the emission spectra and the decay times for a series of uranium–mica compounds including the synthetic and natural autunites are reported. In addition to the conventional decay time measurement, the life times of the six resolved bands have been measured separately for a sample of Mg-containing uranium–mica.

Experimental

Samples. Samples were prepared according to the literature.[8,9] The general formula of uranium–micas is given[10] as $M(UO_2)_2(XO_4)_2 \cdot nH_2O$, where M is an univalent metal ion (M^I_2) or a bivalent metal ion (M^{II}), XO_4 is a phosphate PO_4^{3-} or arsenate AsO_4^{3-}. The prepared samples are those with M=Na_2, K_2, $(H_3O)_2$, Ca, Mg, Sr, Ba, and Zn. The number of water molecules *n* varies according to the condition of the samples; natural autunites with bivalent metal ions have values of ranging from 8 to 12, while those with univalent ions have, to some extent, a lower value of *n*.

The samples were prepared by mixing the solutions containing the component ions and adjusting the temperature and pH at the appropriate values. The procedure for the preparation of $Ca(UO_2)_2(PO_4)_2 \cdot nH_2O$ is given here as an example. The reagents used were of guaranteed grade. Diluted (1.48 mol/l) phosphoric acid (5 ml) was added to a solution of $CaCl_2$ (s.g.=1.25, 500 ml), followed by boiling and the slow addition of about 10 ml of uranyl solution containing 3.7 g of $UO_2(NO_3)_2 \cdot 6H_2O$. The resultant solution was kept warm on a water bath, and the required precipitate was obtained at the bottom of a beaker in approximately 1 h. The samples were confirmed by X-ray diffractometry.

Apparatus. A block diagram for the measurement of the luminescence decay time is shown in Fig. 1. The main part of the system is composed of a microcomputer (TK-80, NEC Japan, 8080 type) and digital counters. All interface units including the digital counters have been hand-made in this laboratory within the expense of one hundred and sixty thousands yen. The microcomputer system with peripheral interfaces is connected on line to the optical system, for which some units of the multi-purpose spectrometer (SS-25, JASCO Japan) are employed. The apparatus is able to measure a wide range of decay times at weak intensity. More details of the system, especially concerning the hardware will be reported later. The measurement of emission spectra and decay times were made at room temperature.

Results and Discussion

According to McGlynn and Smith,[5] the ground state configuration of the UO_2^{2+} molecule is expressed as $(1\sigma_u^+)^2(1\sigma_g^+)^2(1\pi_u)^4(1\pi_g)^4$, leading to a totally symmetric singlet ground state $^1\Sigma_g^+$. The resolved absorptions between 20500 and 30000 cm^{-1} (visible to near UV) occur because of transitions from the ground state to the lowest excited state $^3\Pi_u$, which is split into twelve sublevels due to the symmetric stretching in the excited state (Fig. 3). The luminescence appears to occur from the lowest one or two sublevels to the ground state which is also further split due to the symmetric stretching in the ground state.[4] Figure 2 shows the emission spectra of a synthetic sample of $Mg(UO_2)_2(PO_4)_2 \cdot nH_2O$, which gives a typical spectral pattern for a series of uranium–micas prepared here. Excitation by UV light of 365 nm was found more efficient for the measurement of luminescence than 254 nm, which is understood since the closely separated sublevels arising from the triplet $^3\Pi_u$ efficiently absorb the exciting energy of 365 nm (27400 cm^{-1}), while there is not any appropriate absorbing level for 254 nm (39400 cm^{-1}) (Fig. 3).

The spectra is apparently composed of six bands with an appoximate intensity ratio of 3 : 13 : 45 : 100 : 95 : 8. Peak positions for all the prepared samples are listed in Table 1, together with the life time data. The average spacing of the five lowest energy bands

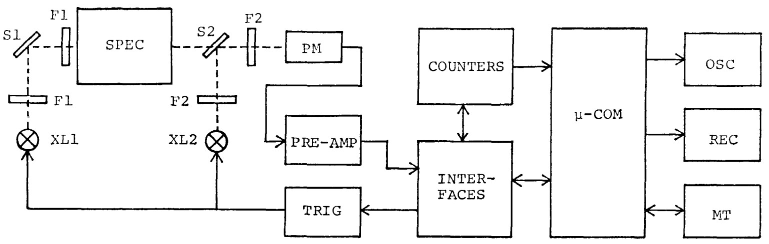

Fig. 1. Block diagram showing the measuring system of luminescence life time. Either the combination of (XL1, F1, S1, F1) or (XL2, F2, S2, F2) is used in the actual measurement.
XL1, XL2 : Xenon lamps, F1, F2 : filters, S1, S2 : samples, SPEC : spectrometer, PM : photomultiplier, TRIG : trigger circuit, μ-COM : microcomputer, OSC : XY-oscilloscope, REC : XY-recorder, MT : magnetic tape.

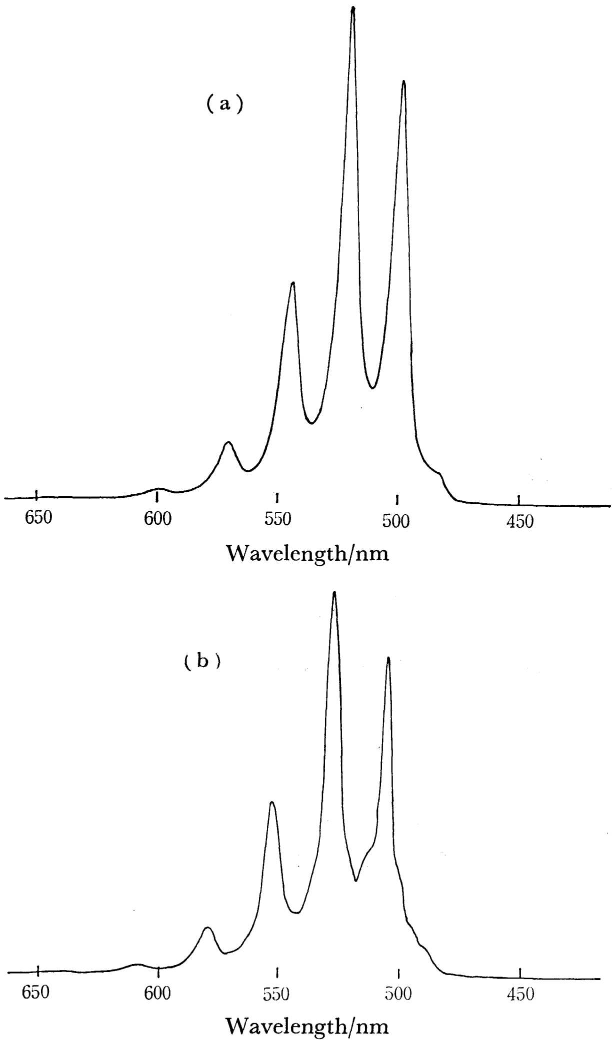

Fig. 2. Emission spectra at the excitation of UV (365 nm) light for $Mg(UO_2)_2(PO_4)_2 \cdot nH_2O$ (a), and for $(H_3O)_2(UO_2)_2(AsO_4)_2 \cdot nH_2O$ (b), where the additional bands are observed.

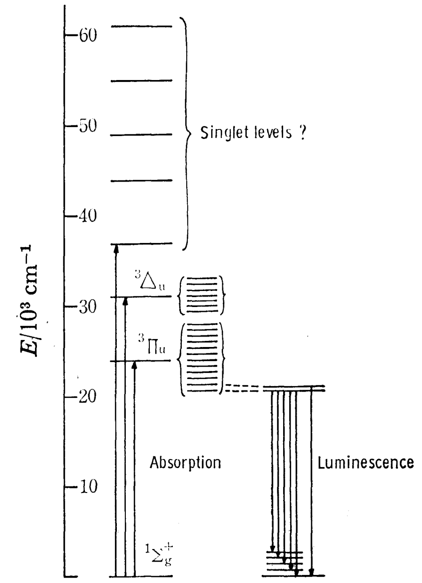

Fig. 3. Energy level diagram for uranyl(VI) ion based on Bell and Biggers' paper.[6)]

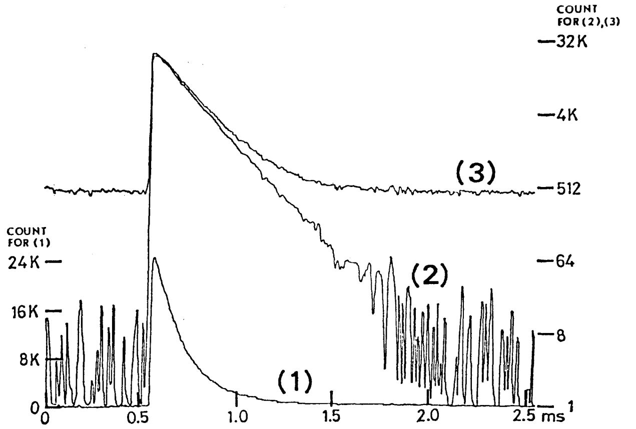

Fig. 4. Decay curve of $Mg(UO_2)_2(PO_4)_2 \cdot nH_2O$ (1) and it's logarithmic conversions with (2) and without (3) background subtraction.

is 840±20 cm^{-1}, while the band at the highest energy is spaced only 710±40 cm^{-1} from the next lower energy band. Bell and Biggers reported the same spectral feature for the emission bands of uranyl(VI) perchlorate in water.[6)] In that case the average spacing for the five lowest energy bands was 855±20 cm^{-1}, while another band was spaced 768 cm^{-1} from its neighbor. They suggested that the latter band is probably from a different origin to the other five emission bands, that is, from the second absorption level. The smaller spacings of the uranium-mica

TABLE 1. EMISSION BAND POSITION AND LIFE TIME OF URANIUM-MICAS

Sample	Life time $\tau/10^{-4}$ s		ν_1[a)]	ν_2	ν_3		ν_4			ν_5			ν_6
$Ca(UO_2)_2(PO_4)_2\cdot nH_2O$	1.9, 2.1[b)]		604	576	550		527			505			488
$Sr(UO_2)_2(PO_4)_2\cdot nH_2O$	3.5, 3.6	(633)[c)]	602	575	549		527			506			488
$Ba(UO_2)_2(PO_4)_2\cdot nH_2O$	2.8, 2.9		604	576	551	545	527			504		(494)	486
$Ba(UO_2)_2(AsO_4)_2\cdot nH_2O$	1.9	(638)	608	579	554		531			509	(500)		(493)
$Mg(UO_2)_2(PO_4)_2\cdot nH_2O$	2.5		600	572	544		523			500			484
$Mg(UO_2)_2(AsO_4)_2\cdot nH_2O$	0.57, 0.7	(636)	603	575	550		526			504			(488)
$Mg(UO_2)_2(PO_4)_2\cdot nH_2O$: Mn(0.03 mol %)	1.3	(631)	599	571	547		523			501			483
$Zn(UO_2)_2(PO_4)_2\cdot nH_2O$: Cu(0.1 mol %)	0.81		602	575	549		525			503			487
$Na_2(UO_2)_2(PO_4)_2\cdot nH_2O$	1.6, 2.2		604	575	549		526			504			486
$Na_2(UO_2)_2(AsO_4)_2\cdot nH_2O$	0.87		607	578	552	546	528	523		506	500		(490)
$K_2(UO_2)_2(PO_4)_2\cdot nH_2O$	2.7, 2.9		603	575	549		526			504			487
$K_2(UO_2)_2(AsO_4)_2\cdot nH_2O$	0.95, 1.1		607	579	553		529			507	(499)		491
$(H_3O)_2(UO_2)_2(PO_4)_2\cdot nH_2O$	—	(636)	602	573	547		523			500			481
$(H_3O)_2(UO_2)_2(AsO_4)_2\cdot nH_2O$	1.3	(640)	609	580	553	537	528	521	514	506	499	495	489
Natural autunite	2.5, 2.6, 2.8		605	575	550		527			505			488

a) ν_1 to ν_6 correspond to the six emission bands after Bell and Biggers.[6)] b) Data obtained at a different run of measurement on the some sample. c) Data in the parentheses are less reliable than others.

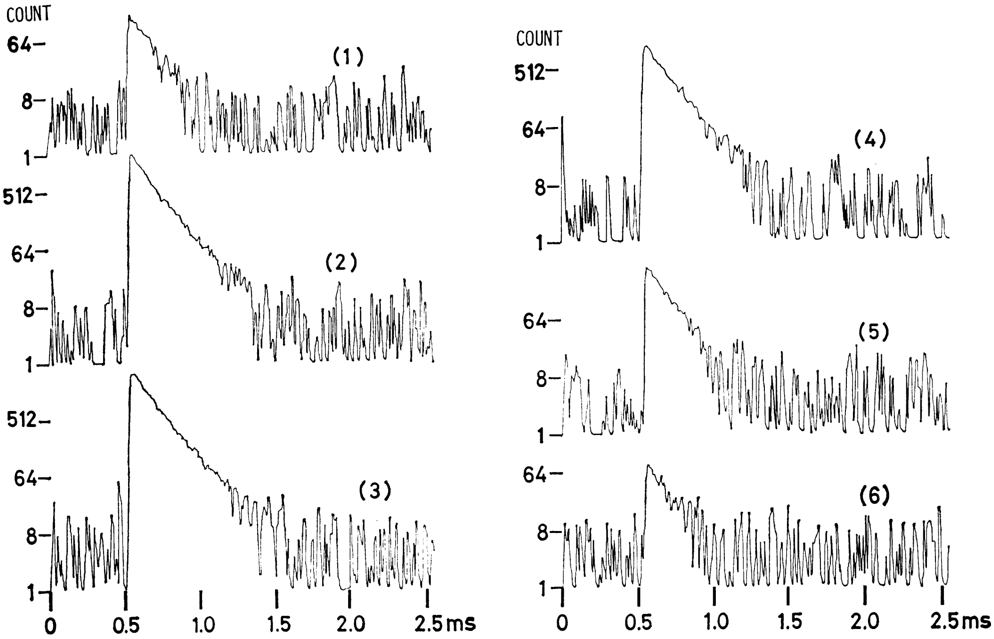

Fig. 5. Logarithmic converted decay curves for bands at 484 nm (1), 500 nm (2), 523 nm (3), 544 nm (4), 572 nm (5), and 600 nm (6) of $Mg(UO_2)_2(PO_4)_2\cdot nH_2O$.

samples compared to those of uranyl(VI) perchlorate in water may be considered as reflecting the geometry of coordination of ligand molecules around the uranyl(VI) ion.[11)]

Decay curves for the six emission bands have been recorded as shown in Fig. 5, where the logarithmic converted lines instead of the direct decay curves are given for convenience. Life time data obtained for the most intense band at 19011 cm^{-1} have the value of 2.5×10^{-4} s, which agrees with the five others within experimental error suggesting that the six emission bands emerge from the same transition mechanism.

As seen in Table 1, some of the samples have additional weak bands besides the six main bands, one of which was observed as a very weak band at the low energy side with the same spacing as the five bands. The others were observed either as shoulders or as asymmetrics of the main bands. Iimori and Iwase[7)] found sixteen emission bands for a natural autunite using a photo technique in almost the same energy region as that of the six bands found here. The sixteen bands were arranged into three series, E(seven bands, very intense), B(five bands, dim), and H(four bands, very dim), each of which has the same wave-number interval of 800 cm^{-1}. The six highest energy bands in the E series coincided well with the six bands reported here.

The remaining band in the E series at the lowest energy (635 nm) found its counterpart only as a very weak and broad band in the spectra recorded here (Table 1). The shoulder bands which were found, for instance, in the spectra of $(H_3O)_2(UO_2)_2(AsO_4)_2 \cdot nH_2O$ could be related to some bands in the B or H series. However, the imprecise energy position and the limited number of shoulder bands do not allow a precise comparison between the bands. The presence of the additional bands, however, is thought to necessitate a more rigorous discussion concerning the origin of the emission bands than has hitherto appeared.[5,6]

The value of n and the changes found during measurement were not recorded however in the present study, since no significant changes were observed in the spectral patterns and in the life times during repeated measurements. The reason for this is presumably that the water molecules in the uranium–micas are located in the cavities in the $[(UO_2)(XO_4)]_n$ layer structure and having a zeolitic water character, they exert only a small influence on the UO_2 energy levels as perturbing ligands.[9]

The replacement of PO_4 by AsO_4 causes a shortening of the life time as well as a shift of the emission bands to low energy about 100 cm^{-1} in the uranium–micas of Ba, Mg, Na_2, and K_2 but the explanation of this remains unknown. It does not seem, however, to be due to paramagnetic impurities contained, for instance, in aresenic acid used in the experiment, since the doped sample of Mg-containing uranium–mica (Mn 0.03 mol %) shows a shortening in life time as a result of the transfer of the absorbed energy to the paramagnetic ion Mn^{2+}, while it does not show any band shift with respect to the sample without paramagnetic impurities.

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