Spectroscopy of U^{3+} in fluoride glasses

LETTER TO THE EDITOR

Spectroscopy of U³⁺ in fluoride glasses

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Abstract. Trivalent uranium ions have been introduced into fluorozirconate and fluoro-aluminate glasses and have been identified using EPR, optical absorption and photo-luminescence spectroscopy. The results are interpreted in terms of an energy level scheme similar to that for U³⁺ in CaF_2. The potential of this system as a laser operating near 2.6 μm is discussed.

Zirconium-fluoride-based glass fibres are possible candidates for low-loss optical fibre telecommunications and have their lowest attenuation at 2.55 μm. To utilise this window fully, a suitable signal generator at this wavelength is required. It has been suggested [1] that U³⁺ might be a suitable lasing ion although it was pointed out that this valence state could be hard to achieve in fluoride glass.

Laser action has been reported from U³⁺ ions in BaF_2 [2] and CaF_2 [3] between 2.5 and 2.6 μm. The transition involved is from $^4I_{11/2}$ to $^4I_{9/2}$ levels. In BaF_2 at 20 K pulsed laser action was obtained with wavelength 2.556 μm (3912 cm^{-1}), but at 77 K lasing was not observed even with 2 kJ input power. This was attributed to the appreciable population of the terminal level because it was only 107 cm^{-1} above the ground state. In CaF_2 lasing was observed at 2.613 μm (3831 cm^{-1}) under pulsed excitation up to room temperature, and CW below 80 K. The reason for the superior lasing characteristics in this host is that the terminating level is 602 cm^{-1} above the ground state and therefore less populated than in BaF_2. The ground-state splitting is sufficiently large to allow lasing on another transition terminating on the first Stark $J = \frac{9}{2}$ level 190 cm^{-1} above the ground state under high excitation conditions. SrF_2 is an intermediate case, with a terminating level 334 cm^{-1} above the ground state, and lasing at 2.407 μm (4155 cm^{-1}) up to 90 K [4].

U³⁺ is an unusual oxidation state in fluorides, the most stable being U⁴⁺ and U⁶⁺. It has never been reported in glasses of any type previously although there are reports of its existence in molten fluoride systems induced by such techniques as linear sweep voltametry [5] and H_2/metal reduction [6].

The purpose of this Letter is to report the observation of U³⁺ in two fluoride glasses using optical spectroscopy and electron paramagnetic resonance (EPR) for identification. The possible application of the glasses as a laser for fluoride glass optical systems is assessed using luminescence spectroscopy. The ions U⁴⁺, U³⁺ and U²⁺ all absorb at many wavelengths throughout the spectral range. However, the U⁴⁺ spectrum in molten

fluorides is well known [7]. As the longer-wavelength absorptions for both U^{3+} and U^{2+} are due to f–f transitions and therefore shielded from environmental effects, they should be similar in different hosts, so these absorptions have been identified by comparison with spectra in crystalline hosts and in melts. The EPR identification of U^{3+} is particularly clear as the even valence states are diamagnetic and should give no signal.

We now describe the experimental procedure. Glasses have been prepared with a range of compositions and melting conditions. However in this Letter the properties of just two of these are discussed, which will henceforth be referred to as the fluorozirconate glass and the fluoroaluminate glass. The composition of the fluorozirconate glass was (mol%) $57ZrF_4$, $35BaF_2$, $3LaF_3$, $4AlF_3$, $1UF_4$ and that of the fluoroaluminate was (mol%) $35AlF_3$, $15YF_3$, $20CaF_2$, $10MgF_2$, $10SrF_2$, $10BaF_2$, $0.1UF_4$. Batches of the base glass were made by weighing and intimately mixing high-purity fluoride powders in a dry box. Uranium in the form of UF_4 was added to the powder in the crucible. A detailed account of the melting and reducing conditions used will be published at a later date. The reduced glass was cast in a brass mould heated to $\simeq 20$ °C below T_g and annealed for about an hour at this temperature. The resulting glass discs were polished parallel under paraffin using cerium oxide.

A Perkin–Elmer UV–visible spectrometer was used to record the room-temperature absorbance between 185 nm and 2600 nm. Luminescence measurements were carried out using the 476.5 nm line from an argon-ion laser for excitation, with unfocused powers of 100 mW. The sample was cooled in an Oxford Instruments CF1024 helium-flow cryostat for the measurements at 10 K. The emitted light was chopped at 400 Hz and passed through a monochromator to an InAs detector. A Nernst lamp provided a black-body source for the system response correction. The same cryostat, lamp and detection system was used to make low-temperature infrared absorption measurements. EPR measurements were carried out using a Varian 4502 X-band spectrometer fitted with an Oxford Instruments helium-gas-flow cryostat.

We will now discuss the optical absorption results. Figure 1 shows examples of typical room-temperature absorption spectra for samples produced under normal melting conditions, i.e. oxidising atmosphere, and under extreme conditions of reduction. These spectra are typical of those reported previously for U^{4+} and U^{3+} in molten fluorides and crystals. There is considerable overlap of spectral features in the visible region, making definite assignments to particular transitions and quantitative analysis of concentrations difficult. Nevertheless the comparison shows that uranium is present predominantly as U^{4+} in the oxidised glass and as U^{3+} in the reduced glass.

From a practical point of view the number of absorption bands in the visible may be an advantage, since they provide several comparatively broad excitation bands for laser pumping. In particular, the U^{3+} bands near 800–900 nm would match both Kr flash or GaAlAs laser pumps.

In the infrared region there are fewer transitions, and in view both of this simplicity and of our interest in the lasing transitions between the two lowest multiplets we have made more detailed absorption measurements at low temperatures, which are shown in figure 2. The main features are due to transitions from the $J = \frac{9}{2}$ ground state to the $J = \frac{11}{2}$ Stark split levels near 4600 cm^{-1}, to the $J = \frac{3}{2}$ levels near 7400 cm^{-1}, and to the $J = \frac{13}{2}$ levels near 8500 cm^{-1}. These assignments are obtained by comparison with the free ion [8]. Each group should split under the crystal field into a maximum of $J + \frac{1}{2}$ Kramers doublet levels, although the variety of local sites broadens them into continuous bands; nonetheless, structure is visible and the expected doublet nature of the 7400 cm^{-1} feature is particularly clear. Photoluminescence excitation into this band may be possible
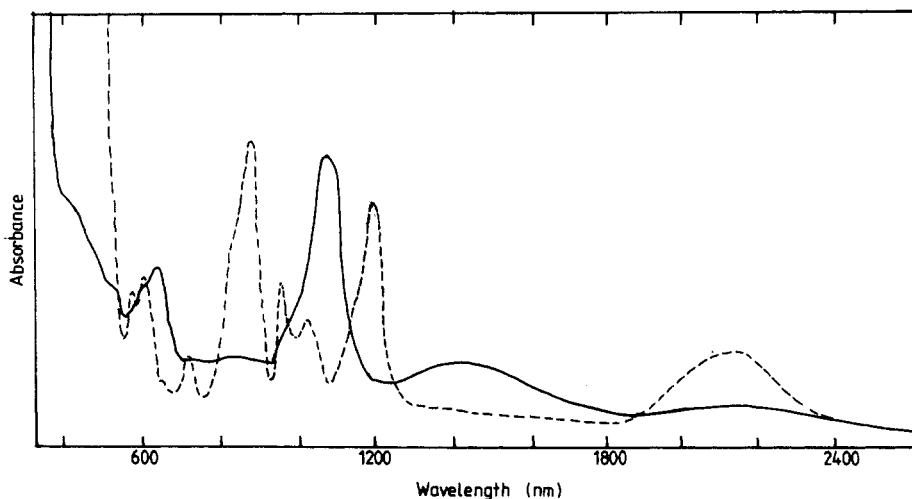
Figure 1. Room-temperature absorption spectra for uranium-doped fluoroaluminate glass samples made under normal (full curve) and reducing (broken curve) conditions.
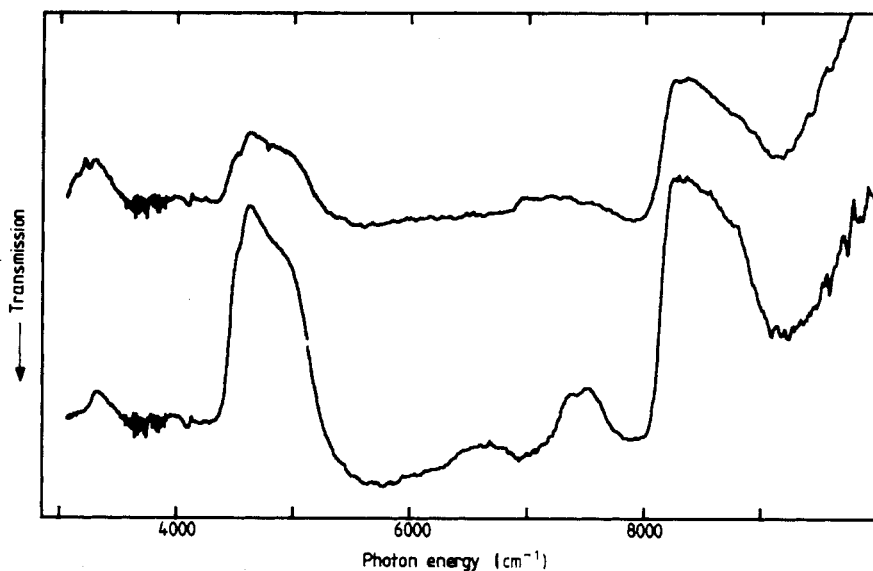
Figure 2. Transmission spectra at 50 K for (*a*) fluoroaluminate glass, (*b*) fluorozirconate glass.

with InGaAsP diode lasers. Though the anticipated six bands in the 4500–4600 cm^{-1} region are not resolved, the two lowest-energy features appear to be near 4510 and 4620 cm^{-1}. The former is from the ground state to the lowest Stark level of the $J = \frac{11}{2}$ multiplet.

There is uncertainty about the origin of the bands near 6700 and 3400 cm^{-1}. The former seems to appear only in the most reduced samples, and so could be due to U^{2+}, although we would then expect a band around 4000 cm^{-1} which is not clearly seen. The later is most probably due to hydroxyl ions.
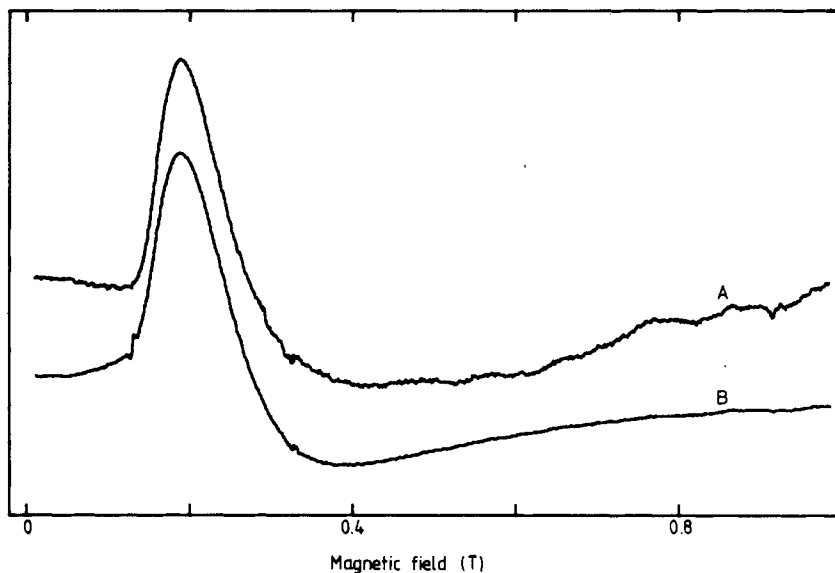
Figure 3. EPR spectra at 20 K using a frequency of 9.17 GHz. (a) U^{3+} in fluorozirconate glass. (b) Nd^{3+} in a ZBLAN glass.

We now consider the EPR results. An asymmetric EPR line was observed in the reduced uranium-doped fluorozirconate glass as shown in figure 3(a). This lineshape is characteristic of a doublet ground state with a highly anisotropic g-value. It is virtually indistinguishable from that of Nd^{3+} in a doped ZBLAN glass, shown in figure 3(b), with low-field derivative peaks at $g = 3.49 \pm 0.02$ for both ions. Nd^{3+} and U^{3+} have configurations $4f^3$ and $5f^3$ respectively and are expected to give similar EPR signals; these have been reported in crystalline materials such as $LaCl_3$ [9, 10].

EPR not only confirms the presence of U^{3+} but also affords a method for the absolute determination of the U^{3+} concentation. This has been carried out by comparing the EPR signal strengths from the weighed uranium-doped sample with that from a neodymium-doped glass sample of accurately known concentration. The method assumes that the lineshapes, and hence the g-values and transition probabilities are identical for the two ions. The observed lineshapes indicate that this is a reasonable assumption. The molar concentration of U^{3+} in the fluorozirconate sample by this method is 0.6 mol%, showing that the majority of uranium is in the reduced state. No measurable EPR was observed from the fluoroaluminate sample which had a much lower total uranium concentration.

Neither glass shows evidence for the presence of Zr^{3+}. The characteristic EPR signal reported in other reduced glasses [11] was not seen in either of the present samples. Nor did the optical measurements reveal the broad absorption centred on 450 nm attributed to this ion when produced in fluoride glass by irradiation.

We now go on to consider the photoluminescence results. Figure 4 shows the photo-luminescence spectra of the fluoroaluminate and fluorozirconate glasses taken at low temperatures in the region of the U^{3+} $J = \frac{11}{2}$ to $J = \frac{9}{2}$ transition. Although the latter contains more U^{3+}, its efficiency is lower because of its poorer optical quality. Luminescence spectra can readily be measured at room temperature. From the lowest temperatures to room temperature, the integrated efficiency is almost constant for the fluoroaluminate and is reduced by no more than a factor of five in the fluorozirconate.
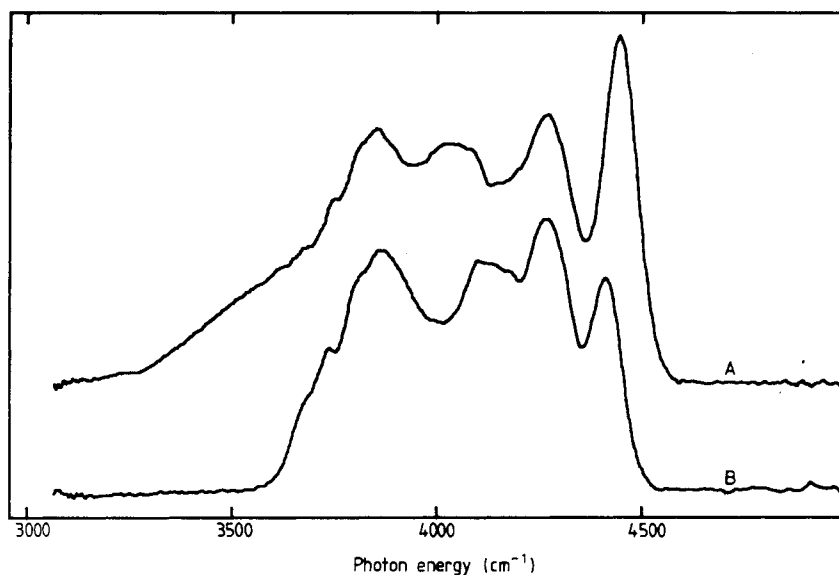
Figure 4. Photoluminescence spectra using 476.5 nm excitation. (*a*) Fluoroaluminate glass at 7 K. (*b*) Fluorozirconate glass at 9 K (gain × 2).

In the fluoroaluminate the highest-energy transition is, like the other spectral features, largely unaffected by temperature, and peaks close to 4445 cm^{-1}. It is likely that this transition is to the first excited $J = \frac{9}{2}$ Stark level and that the sharp high-energy edges seen in both glasses are due to self-absorption by the transition from the lowest $J = \frac{9}{2}$ level. The latter is seen in absorption at 4510 cm^{-1} but not in emission, suggesting it is totally self-absorbed. The proposed energy level scheme for the fluoroaluminate is shown in figure 5; the fluorozirconate differs only in detail. This scheme accounts for the five levels expected for the $J = \frac{9}{2}$ multiplet in a low-symmetry environment.

It is instructive to compare these energies with those of U^{3+} in the well-defined crystalline environments of alkaline-earth fluorides. Such comparisons show without doubt that we have trivalent uranium ions in our glasses, and that the energy level distribution most closely resembles that in CaF_2. For the fluoroaluminate sample, the transition between the lowest $J = \frac{11}{2}$ and $J = \frac{9}{2}$ level is at 4510 cm^{-1}, compared with 4433 cm^{-1} in CaF_2 [12]. This energy changes little in a variety of fluoride hosts: the early work of Galkin and Feofilov [13] at 123 K finds 4505 cm^{-1}, 4545 cm^{-1} and 4565 cm^{-1} in CaF_2, SrF_2 and BaF_2 respectively. The overall Stark splitting of the $J = \frac{9}{2}$ multiplet (660 cm^{-1}) in the glass is somewhat larger than that in CaF_2 (602 cm^{-1}) [12].

In conclusion, it has been shown that it is possible to produce uranium-doped fluoride glasses in such a way that the majority of the dopant ions are in the trivalent state. These ions have been identified through their EPR, optical absorption and photoluminescence spectra, the EPR also providing estimates of the concentration. The luminescence data suggest that the energy level structure of the lower-lying states is similar to that of U^{3+} in CaF_2.

Since CaF_2:U^{3+} is a known laser medium operating CW at low temperature and pulsed at room temperature, we anticipate laser characteristics at least as good for the fluoride glass host. It is possible that the solubility limit is higher in the glass, leading to higher-energy densities, as is the case in the Nd:YAG and Nd:phosphate glass systems.
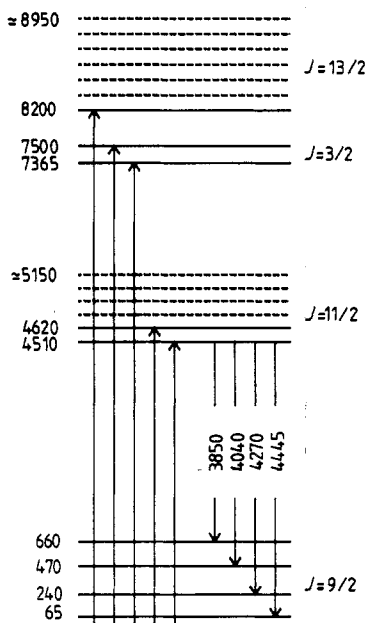
Figure 5. Proposed energy level scheme for U^{3+}, from measurements appropriate to the fluoro-aluminate glass, showing transition frequencies in cm^{-1}. Full lines show resolved levels, broken lines are unresolved levels drawn within the observed absorption band width. (Not to scale.)

The spectra indicate greater crystal-field splittings in the glass. This, together with the observation of only weakly temperature-dependent luminescence efficiencies, suggests that higher CW working temperatures may be achievable. The expected laser transition is at about 3850 cm^{-1} (2.6 μm), very close to the fluorozirconate glass attenuation minimum. The absorption spectra also identified two groups of potential pumping levels suitable for flash lamp and laser diode sources.

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