Unusual Luminescence of Titanium(III) in Aluminium Oxide**

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Abstract: Titanium(III) in corundum shows a short-lived (3.1 μs) broad $^2E - {}^2T_2$ luminescence around $\lambda = 740$ nm, and a 10 times longer-lived $^2A_1$ ("4s") – $^2T_2$ centered around $\lambda = 410$ nm. Both these broad-band emissions with large Stokes shift offer prospects for tunable lasers. The absorption spectrum has been studied in detail, and traces of titanium (IV) are shown not to be involved in the "violet" emission, in contrast to a parasitic absorption around $\lambda = 700$ nm due to $Ti^{III,IV}$, like sapphire is blue due to $Fe^{II}\ Ti^{IV} \rightarrow Fe^{III}\ Ti^{III}$ electron transfer bands.

Corundum, the α-modification of Al_2O_3, has almost exactly regular octahedral sites for the cation, though spectroscopic characteristics in polarized light clearly indicate the uniaxial hexagonal crystal type. Those trivalent ions which form hydrated alums can be incorporated on the octahedral site, and for instance Al_2O_3, Cr_2O_3, and Fe_2O_3 are fully miscible. The absorption spectra of trivalent 3d-group ions in corundum were studied[1] when the first laser, the ruby $Cr_xAl_{2-x}O_3$ with $x \approx 0.01$, was operated in 1960. Though the colorless corundum (nearly as hard as diamond, and used in optical components transparent in the far ultraviolet) frequently is called sapphire, this blue mineral contains simultaneously small amounts of iron(II) and titanium(IV) on the octahedral sites, and the broad absorption band[2,3] at $\lambda = 575$ nm with a shoulder at $\lambda = 720$ nm is due to electron transfer forming, to the first approximation, $3d^5$ iron(III) and $3d^1$ titanium(III) in the excited state, as frequently found[4–6] in compounds containing iron(II) at short distances from oxidizing ions, including iron(III). The black mineral ilmenite, $FeTiO_3$, has an ordered super-structure of corundum. It may be noted that ilmenite-type $Ni_xMg_{1-x}TiO_3$ and $Ni_xCd_{1-x}TiO_3$ were studied by *Reinen*, allowing important conclusions[7] about the $3d^8$ states of nickel(II) corresponding to the absorption bands.

Some lasers, based on gaseous atoms or positive ions, emit spectral lines. This is almost true also for lanthanoide salts containing a partly filled 4f shell[8,9]. On the other hand, fluorescent organic colorants in solution, or excimer lasers based on ephemeric diatomic molecules in gases, emit broad luminescence bands, and under favourable conditions, can be used for *tunable* lasers, such as certain cases of $3d^3$ chromium(III) emitting a broad band in the near infrared from the first excited quartet state $^4T_2$ to the electronic ground state $^4A_2$. Since $^4T_2$ has one strongly anti-bonding d-like electron, the Franck-Condon principle demands the co-excitation of a broad vibronic continuum belonging to the ground state. The situation is quite different in the narrow-band emission of ruby, where the first doublet state ^2E involves the same three roughly non-bonding electrons as $^4A_2$. Tunable lasers emitting from $^4T_2$ in the isoelectronic vanadium(II) incorporated in rutile-type $V_xMg_{1-x}F_2$ have been studied[10] but present difficulties of black-out due to color centres formed during large-scale operation.

Titanium(III) has one 3d electron which can be excited (by light close to $\lambda = 500$ nm) to the two anti-bonding orbitals with angular functions proportional to $(x^2 - y^2)$ and $(3z^2 - r^2)$. If the octahedron TiX_6 was exactly regular, these two orbitals would have identical energies. Actually, the hexaaqua ion in acidic, non-complexing solutions[11,12] shows a shoulder at $\lambda = 575$ nm on the asymmetric peak at $\lambda = 492$ nm. This can hardly be ascribed to a distorted environment, as would be conceivable in a doped crystal (especially in the case of quite differing ionic radii). It may be relevant that the isoelectronic vanadium(IV) forms the highly anisotropic[12,13] blue vanadyl aqua ion $OV(OH_2)_4^{2\oplus}$ containing its unpaired electron in the orbital (xy) which is the only non-bonding 3d orbital in the case of strong π-anti-bonding effects of oxo ligands on the z Cartesian axis. The diamagnetic ground state of MO_2X_4 complexes[14] of M = ruthenium(VI), rhenium(V), and osmium(VI) corresponds to two electrons in (xy).

It is generally argued that the splitting of the visible absorption band of titanium(III) is due to the Jahn-Teller effect. The slightly problematic side of this explanation is that Jahn-Teller-stable ground states do not provide band splittings by transitions to even highly separated potential surfaces in the 16-dimensional space corresponding to 7 nuclei in MX_6[13]. However, a quite weak deviation from O_h in the ground state can produce strong energy separations by Franck-Condon projection on high-lying potential surfaces, much in the same way as the width of "ligand field" absorption bands, though originating in the thermal (and zero-point) vibration[15], frequently is 10 times kT, and largest for the lightest ligands. In the octahedral d-group complexes, the typical cases of strong Jahn-Teller splitting occur for unbalanced occupation of $(x^2 - y^2)$ and $(3z^2 - r^2)$ in the ground state, actually by 0 and 1 electron in the quintet ground states of $3d^4$ chromium(II) and manganese(III); and by 1 and 2 electrons in $3d^9$ copper(II). A few instances are known[16] of pronounced band splitting of iron(II) hexa-aqua ions and in the quintet ground state hexafluoro complex of cobalt(III). Since the two σ-anti-bonding orbitals have each one electron, the phenomenon is here ascribed to Jahn-Teller effect in the (at most) π-anti-bonding (xy), (xz), and (yz) accommodating 4 electrons. It is known from chromium(III) complexes[17] that π-anti-bonding effects are up to 30 percent of the σ-anti-bonding effect, the highest ratio is observed for fluoride ligands. Hence, it can be concluded that the weak Jahn-Teller effect on titanium(III) is induced by the π-anti-bonding only. Because of the mechanism of the Stokes shift, the consequences are likely to be more pronounced for luminescence than for absorption. Jahn-Teller effects for the excited $^4T_2$ of chromium(III) in cubic crystals have been detected[18] in the vibrational fine-structure (below 10 K) of the broad emission band.

Powell et al.[3] recently studied the absorption and emission spectra of $Ti_xAl_{2-x}O_3$ and found an asymmetric band (we find the maximum at $\lambda = 483$ nm and a shoulder at $\lambda = 550$ nm) surprisingly similar to the aqua ion in alums[11] and in acidic solutions. The near-infrared emission occurs in

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a broad band around $\lambda = 740$ nm, satisfying one of the necessary conditions for tunable lasers[10]. This emission in corundum has been studied by two other groups[19–21] and one of the difficulties for obtaining a positive amplification along the laser path is a somewhat unpredictable absorption between $\lambda = 700$ and 850 nm. Though it is difficult to study trace impurities in crystals almost as hard as diamond, it does not seem to be Fe^{II}, Ti^{IV} providing the blue color of sapphire[3] but rather adjacent $Ti^{III,IV}$ sites known[12] in 12 M hydrochloric acid, where simultaneously present (very pale yellow) Ti^{IV} and a sky-blue Ti^{III} chloro complex (with maximum at $\lambda = 525$ nm) form a dark brownish-purple 1:1 complex with a 8 times stronger, broad band at $\lambda = 482$ nm, having a shoulder at $\lambda = 670$ nm. The formation constant of this complex is 12 M^{-1} showing a pronounced affinity between the two (chloro-bridged) oxidation states. The diagnosis is that parasitic absorption can be avoided in titanium(III) doped corundum if all traces of Ti^{IV} can be reduced to Ti^{III}, or at least kept at large average distance from the Ti^{III} providing the main absorption.

As described in the experimental section, we studied three crystalline samples, among which one (R 10) does not present the flat background absorption slightly decreasing from $\lambda = 650$ to 850 nm, as do the samples R 4 and R 8. In all three samples, excitation at $\lambda = 488$ nm, monitoring emission at $\lambda = 732$ nm, and also in R 10 excited at 488 nm and monitored at 650 and 850 nm, the decay curve (after an initial rise-time of $3 \cdot 10^{-7}$ s suggesting rapid energy transfer from states producing much stronger ultraviolet absorption than the "4s" state discussed below) is almost exactly exponential with the life-time (3.1±0.1 μs). This is comparatively short, since the radiative life-time

$$\tau_{rad} = (e_2/e_1)\ 2.3 \cdot 10^{-8}\text{s}/[P(h\nu/\text{eV})^2] \qquad (1)$$

is close to $3 \cdot 10^{-5}$ s for the Ti^{III} aqua ion[15] having the oscillator strength $P = 1.2 \cdot 10^{-4}$ if the debatable ratio between e_2 excited states and e_1 states in the ground level is put equal to 1. As seen in the experimental section, the ε values at $\lambda = 488$ nm for Ti^{III} in corundum are closely similar to 4.1 for the aqua ion in solution, as well as the shape of the absorption band. Hence, it seems that the order of magnitude for the quantum yield of near-infrared luminescence is close to 0.1.

A much more spectacular luminescence of all three samples is a broad emission band (Fig. 1) having the maximum at $\lambda = 410$ nm and half the peak intensity at $\lambda = 365$ and 460 nm. This "violet" emission was already reported by *Powell* et al.[3] at $\lambda = 420$ nm with observed life-time $\tau = 2.3$ μs. As seen in Table 1, we find life-times gliding from 15 toward 35 μs for most of the emission wave-lengths studied, for excitation of all three samples at $\lambda = 337$ nm. On the other hand, we did not find any dependence on the exciting wavelength of the position and shape of the emission band. The luminescence may very well be due to a superposition of two or several mechanisms, the slowest corresponding to the asymptotic value of τ close to 30 microseconds.

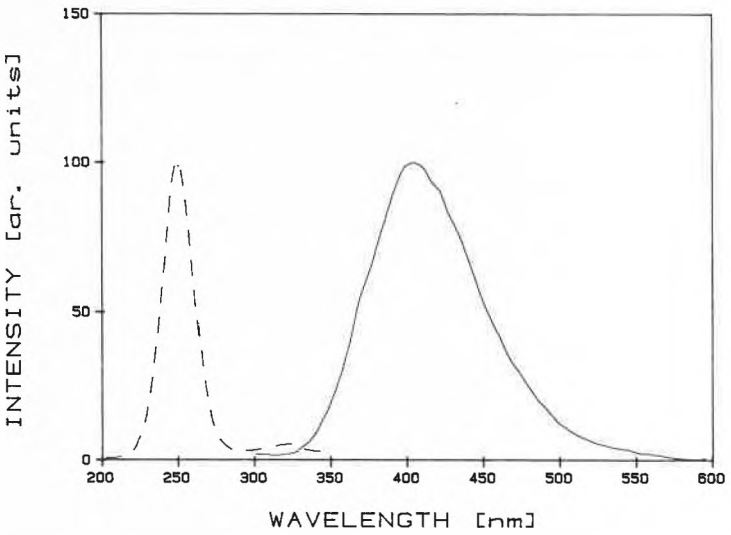

Fig. 1. Emission spectrum (full line; excited in an interval around $\lambda = 265$ nm) and excitation spectrum (dashed line; emission measured at $\lambda = 450$ nm) of sample R 4.

Searching the emitting state, we measured the excitation spectra for emission at $\lambda = 350$, 400, and 450 nm and found in all three samples an (energy-wise) quite broad band at 265 nm. One may feel some doubts whether superposed competing absorption bands shift this excitation maximum at 265 nm from the average position of the emitting state. Going from the absorption maximum toward ultraviolet, the minimum $\varepsilon \approx 2$ occurs at 405 nm, and $\varepsilon = 5$ is crossed close to 310 nm. The subsequent increase is very smooth, and reaches $\varepsilon = 200$ close to 245 nm. There are no evident shoulders between 300 and 250 nm, and $\varepsilon \approx 25$ at 265 nm.

Since mixed oxides containing titanium(IV) absorb very strongly in the near ultraviolet, in contrast to the much less oxidizing zirconium(IV) and thorium(IV), one might expect an electron transfer state of Ti^{IV} producing the "violet" emission in analogy to solid vanadates[22]. This is rendered unlikely by the essentially similar absorption spectra in the ultraviolet, and the emission characteristics, of R 4 and R 8 compared with the sample R 10 lacking near-infrared absorption indicating absence of admixed Ti^{IV}. Hence, the "violet" emission seems to originate in Ti^{III}.

The most attractive hypothesis is a transition of the single 3d electron to a 4s-like orbital. Such a transition may be very weak, and if the asymptotic $\tau \approx 30$ μs is not an artefact of energy trapping[23], equation (1) provides $\tau_{rad} \approx \tau$ for $P = (e_2/e_1) \cdot 4 \cdot 10^{-5}$. Since the quantum yield η cannot be > 1, this is a higher limit for P (which is to be multiplied by η if below 1). This means that the absorption corresponding to "violet" emission is a few times weaker than the band at $\lambda = 483$ nm, and one can hardly hope a contribution to ε below 2 to be detectable below 300 nm.

3d-"4s" transitions have only been detected in compounds of a few reducing d-group ions. The best characterized case[15] is the band of $Fe(OH_2)_6^{2\oplus}$ at 248 nm (40 300 cm^{-1}) having $\varepsilon = 18$ and $P = 3.5 \cdot 10^{-4}$. The position may be compared with the two levels of $3d^5 4s$ of gaseous $Fe^{2\oplus}$, $^7S_3$ situated at 30 089 cm^{-1} and $^5S_2$ at 40 999 cm^{-1} above the $3d^6$ ground state. Two counteracting influences modify the 3d-4s separation: the effective positive charge is smaller[7–9] in the compound; but the 4s orbital is always anti-bonding with respect to any set of ligating atoms, as can be seen from gaseous $Cu^{\oplus}$ of which the levels $^3D_3$ (21 929), $^3D_2$ (22 847), $^3D_1$ (23 998), and $^1D_2$ (26 264) of $3d^9 4s$ are situated the number of cm^{-1} (given in parenthesis) above the closed-shell ground state. These levels may be compared with a band[24] of the newly detected complex $Cu(NH_3)_3^{\oplus}$ at 290 nm (34 000 cm^{-1}) having $\varepsilon \approx 300$, whereas $Cu(NH_3)_2^{\oplus}$ absorbs less and begins at higher energy. The strong dependence of intensities of parity-forbidden transitions on the local symmetry is well-known from internal transitions in the partly filled 3d shell, e.g. of octahedral and tetrahedral cobalt(II) complexes. The 3d-"4s" transitions start at 31 500 cm^{-1} in $Cu_xNa_{1-x}F$ and are quite weak[25].

Besides corundum, there are very few cases known of titanium(III) luminescence. Recently[26], a fluorophosphate glass was studied in Shanghai. The absorption increases strongly below $\lambda = 350$ nm and shows a peak at 529 nm and a shoulder at 685 nm. Excitation at $\lambda = 308$ nm produces a very broad emission centered around 530 nm with τ of order 10 μs at 77 K, but depending to some extent on the emission wave-length, as one might expect from differing sites in the glass[9,23]. It is likely that this green emission with an enormous Stokes shift (from a maximum

Table 1. Life-times in microseconds of "violet"emission of titanium(III) in corundum excited at $\lambda = 337$ nm, and emission measured at the nm value given. τ_n are defined in the experimental section.

Sample	nm	τ_1	τ_2	τ_3
R 4	350	1.8	6.3	10.3
	400	3.1	12.6	19.4
	450	11.7	18.9	24.2
	500	24.1	28.4	29.2
	542	18.8	31.3	30.3
	600	23.7	32.5	29.4
	650	15.2	29.8	30.8
	732	4.2	17.1	28.2
R 8	542	23.1	32.6	29.4
R 10	542	15.7	30.5	34.8

in the excitation spectrum at 290 nm) is analogous to the "violet" emission studied here.

Experimental

The crystals obtained by the VSOM technique previously described[27] were polished with two parallel surfaces typically separated by 1 cm. The samples selected were:
R 4: density $\rho = 3.795$ g/cm^3, nominal titanium concentration $c_{Ti} = 0.01425$ mol/L;
R 8: $\rho = 3.744$ g/cm^3, $c_{Ti} = 0.01425$ mol/L;
R 10: $\rho = 3.928$ g/cm^3, $c_{Ti} = 0.01475$ mol/L.

Steady-state measurements: Absorption spectra were measured of the crystal against air on a Perkin-Elmer double-beam spectrophotometer model Lambda 3. Assuming the c_{Ti} given above, the molar extinction coefficient ε at $\lambda = 488$ nm was found to be 4.5 for R 4; 4.9 for R 8; and 3.9 for R 10. – Emission and excitation spectra were measured with the Perkin-Elmer L3 with a B&L home-made, and a Spex home-made, spectrofluorimeter. Excitation at $\lambda = 265$ nm was performed with radiation from a high-pressure xenon lamp gone through a monochromator.

Life-time measurements: A nitrogen laser (337 nm) was used directly for exciting "violet" emission, and combined with the dye no. 8 emitting at 488 nm for exciting the red and near-infrared emission. Table 1 shows the folded life-time τ_1 (for e^{-1} times the original intensity), τ_2 (half the time for e^{-2}), and τ_3 (a-third the time for e^{-3}), all in microseconds, of the emission studied at wave-lengths between 350 and 732 nm of the three samples.

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