Structural, optical and magnetic resonance properties of TiO$_2$ fibres grown by laser floating zone technique

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TiO$_2$ fibres grown by the laser floating zone technique show the rutile crystalline phase as identified by X-ray diffraction and Raman spectroscopy. Scanning electron microscopy evidences a uniform surface, free of inclusions and without low-angle grain boundaries and bubbles. At low temperatures, the fibres luminescence is dominated by a richly structured optical centre with two well-defined zero-phonon lines at 1.579 eV and 1.574 eV followed by an intense vibronic sideband with a maximum close to 1.47 eV. Electron paramagnetic resonance revealed that substitutional chromium and iron ions are present as contaminants in the grown fibres, alongside with Ti$^{3+}$ interstitials and other structural defects. The chemical nature of the defect responsible for the structured near-infrared luminescence is discussed.

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1. Introduction

Anatase and rutile forms of titanium dioxide have recently attracted much research interest due to their versatile applications in the photocatalysis [1], gas sensing [2], solar cells [3], and light waveguides [4], among others. Moreover, rutile single crystals are an excellent material for polarizing devices because of a large birefringence and good chemical durability [5]. Although nanocrystalline rutile titanium dioxide grown by different routes has been widely studied, the mechanisms that govern the optical and electrical properties in the different crystalline forms are still under debate. The problem awoke a renewed interest in a thorough characterization of intrinsic defects and impurities in bulk TiO$_2$ crystals [6–10].

The growth of bulk crystals by the floating zone (FZ) technique assisted by halogen bulbs has been reported to produce rutile TiO$_2$ single crystals [5,11–15]. The main advantage of this method is the absence of crucibles, thus providing a nearly contaminant-free material. Under a low oxygen pressure, dark-blue oxygen-deficient crystals were obtained [11]. Transparent crystals were achieved in the presence of small amounts of Al$_2$O$_3$ [12], ZrO$_2$ [13] or even in the absence of any doping [5]. Kotani and Fuller [16] were the first to apply the growth technique used in the present work. They have undertaken a study of the influence of the controlled atmosphere on the crystal growth. TiO$_2$ bicrystals were successfully grown and their structural properties studied. However, Kotani et al. did not investigate the optical nor the magnetic resonance spectra of the obtained samples.

In the present work, TiO$_2$ fibres were grown by the laser floating zone (LFZ) technique using a CO$_2$ laser. The growth was performed with different pulling rates in air ambient at atmospheric pressure. As evidenced by electron paramagnetic resonance, all the grown fibres exhibit the presence of substitutional chromium and iron ions, alongside with Ti$^{3+}$ interstitials and other structural defects. Under above-band gap excitation the fibres are optically active showing a main structured optical centre in the near-infrared spectral region. The fibres’ morphological, structural, optical and magnetic resonance properties are reported, and a discussion of the chemical nature of the defects originating the observed luminescence is performed.

2. Experimental details

TiO$_2$ fibres were grown by the LFZ technique using a CO$_2$ laser (10.6 μm, 200 W) as a heat source. Feed and seed rod precursors for the LFZ growth were prepared by mixing a commercial TiO$_2$ powder (99%, Merck) with polyvinyl alcohol (PVA, 0.1 g/ml, Sigma) to keep the powder aggregate. The mixture was further extruded into cylindrical rods with a diameter of 1.5 mm and 100 mm of length. The laser melted the top of the feed rod, and the seed was immersed into the molten zone and pulled upwards at three distinct pulling rates: 5, 10 and 30 mm h$^{-1}$. Fibres with 1.5 mm of diameter and 30 mm of length were obtained in air ambient at atmospheric pressure, rotating the feed and seed rods with 5 rpm in opposite directions.

The fibres’ microstructure was characterized by scanning electron microscopy (SEM, Hitachi S4100) on polished surfaces of longitudinal fibre sections. Additionally, the structural
characterization of the as-grown fibres was obtained by X-ray diffraction (XRD). The sample was mounted on a Hampton Research Cryoloops and data were collected by a Bruker Kappa X8 APEX II coupled to a CCD. The distance between the sample and the detector was 35 mm. Room temperature (RT) Raman spectroscopy (Jobin Yvon T64000) in backscattering configuration using a 532 nm laser line was also performed.

Steady state photoluminescence (PL) measurements were carried out between 14 K and RT using the 325 nm laser line of a cw He–Cd laser as excitation source. The emitted light was dispersed by a Spex1704 monochromator (1 m, 1200 mm−1) and detected with a cooled photomultiplier (Hamamatsu R928).

Electron paramagnetic resonance (EPR) measurements on the grown fibres were carried through in the X-band (9.4 GHz) in a Bruker ESP 300E spectrometer at temperatures ranging from 5 K to 300 K.

3. Results and discussion

Fig. 1(a) shows the typical visual appearance of the LFZ grown fibres. The fibres have a dark blue colour currently associated with oxygen deficiency and interstitial Ti\textsuperscript{3+} ions [5,11]. On the left side of the picture a precursor rod is still observable at the fibre extremity. A SEM micrograph (Fig. 1(b)) of a fibre longitudinal section evidences a uniform surface, free of inclusions, grain boundaries or bubbles. The crystal structure of the fibres was determined by single-crystal XRD as shown in Fig. 2. The data indicate that the fibres crystallize in the tetragonal structure with lattice parameters of $a = b = 4.70$ Å and $c = 3.01$ Å. These are in fair agreement with the ones reported by Mo and Ching [17] ($a = b = 4.59$ Å and $c = 2.96$ Å) for the rutile phase. The observed Laue spots suggest the monocrystalline nature of the sample. Nevertheless, we cannot rule out the existence of crystal domains along the $c$-axis, as evidenced by the EPR results (see below). The Raman spectrum shown in Fig. 3(a) also corroborate the rutile structure. Independently of the used pulling rates, the vibrational modes typical of the rutile crystalline phase were identified at 447 cm\textsuperscript{-1} ($E_g$) and 612 cm\textsuperscript{-1} ($A_{1g}$), as well as the low-frequency two-phonon band [18].

![Fig. 1](image1.png)

Fig. 1. (a) Macrograph view of the TiO\textsubscript{2} fibre grown at 10 mm h\textsuperscript{-1}. Notice the 1 mm background mesh. (b) SEM micrograph of the polished longitudinal cross-section of the same fibre.

![Fig. 2](image2.png)

Fig. 2. Single crystal XRD (Laue) patterns for a TiO\textsubscript{2} fibre grown at 10 mm h\textsuperscript{-1}.

![Fig. 3](image3.png)

Fig. 3. (a) RT Raman spectrum taken in backscattering configuration using the 532 nm laser line for the fibre grown at 10 mm h\textsuperscript{-1}. Similar spectra were obtained for samples grown at 5 and 30 mm h\textsuperscript{-1}. (b) Normalized 14 K PL spectrum for the fibre grown at 10 mm h\textsuperscript{-1} obtained with above-band gap excitation. The spectrum was shifted in energy in order to evidence the vibronic coupling.
At 1.6 K, rutile TiO$_2$ exhibits a fundamental indirect absorption edge at $\sim$3.065 eV for $E$/c, with the direct forbidden transition occurring at 3.031 eV for $E$/c$_{\text{LC}}$ [19,20]. Both the anatase and rutile forms of TiO$_2$ are known to be optically active when excited with above-band gap photons [21–26]. For the anatase structure, the emission is mainly due to a self-trapped exciton recombination which appears as a broad unstructured orange luminescence band [23], while for the rutile phase a broad unstructured band in the near-infrared spectral region is commonly reported. The latter has been attributed to oxygen vacancies and/or Ti$_{\text{3i}}$ interstitials [21,26].

Figs. 3(b) and 4 show the PL spectra of the LEZ-grown TiO$_2$ fibres obtained upon above-band gap excitation. Contrary to the unstructured bands formerly observed in rutile TiO$_2$ [21,26], the near-infrared emission detected in the fibres grown at different pulling rates exhibits narrow zero-phonon lines assisted by a rich vibronic structure (Fig. 4(a)). At 14 K the spectrum exhibits a strong zero-phonon line centred at 1.574 eV (A$^+$) and a weaker one at 1.579 eV (A$^-$ line). On the low-energy side of the A$^+$ line (Fig. 3(b)) a pronounced phonon sideband can be seen with prominent low-energy phonon bands and a strong coupling near the E mode, which is the expected behaviour of an internal d–d transition (e.g. Fe$^{3+}$ in II–VI and III–V hosts [24,27]). An earlier study performed by Grabner et al. [25] reported the same structured luminescence in large single crystals grown by the Verneuil technique. The A lines were assigned to magnetic dipolar transitions corresponding to the intraionic $^4T_{2g} \rightarrow ^4A_{2g}$ recombination of Cr$^{3+}$ ions. The same author [28] reported a $\sim$0.18 meV splitting in the ground state and a $\sim$5.0 meV splitting in the excited state. As shown in Fig. 4(a), the PL intensity of the optical centre was by nearly an order of magnitude higher for the fibre grown at a pulling rate of 10 mm h$^{-1}$ than for the other fibres. The PL intensity is obviously controlled by the presence of nonradiative recombination centres which we are not able to control at the present stage of the growth technology. Thus, we centred our attention on this particular sample. The temperature-dependent PL spectra recorded on the latter are shown in Fig. 4(b) and (c). As the temperature rises, the state involved in the 1.579 eV (A$^+$) emission becomes thermally populated at the expense of the 1.574 eV (A$^-$) line, and at higher temperatures only a broad unstructured band peaked at $\sim$1.5 eV is observed (Fig. 4(b)). Since the relative intensities of the A$^+$ and A$^-$ lines are determined by the Boltzmann distribution between the two emitting levels, the Arrhenius plot (Fig. 4(d)) of their intensity ratio is linear, and an energy separation of $\Delta E = 4.7 \pm 0.1$ meV was obtained, which is in good agreement with the $\sim$5.0 meV splitting of the excited state measured by Grabner et al. [25]. The analysis of the A lines peak positions with increasing temperature reveals, however, a different behaviour from that previously reported. In fact, and contrary to the constant value reported by the authors of Ref. [25], a low-energy shift of the A lines peak positions was identified in the grown fibres at temperatures increasing from 14 K to 65 K (Fig. 4(b)), which is likely to be

![Fig. 4.](image-url)
Fig. 5. Angular dependence of the EPR spectra of the sample grown with 10 mm h⁻¹ taken upon rotation of the magnetic field in the (001) plane at room temperature. The black lines indicate the calculated positions of the Fe³⁺ transitions, and the magenta ones – those of the (strongest) Cr³⁺ transitions.

due to a quadratic coupling to low-energy phonons. Grabner et al. [25] have found a lifetime of 45 µs (both at 4 K and 77 K) for the assigned ⁴T₂g → ⁴A₂g Cr³⁺ transition. Based on this short lifetime, the authors of Ref. [25] assumed that the ⁴T₂g state is the lowest excited energy level rather than the ₂E_g state which is typically responsible for the Cr³⁺ R-lines in several hosts, as, e.g., in Al₂O₃ [29,30]. In fact, a spin-forbidden transition (₂E_g → ¹A₂g) usually has lifetimes in the ms range, and so the measured values were incompatible with the ₂E_g state as the lowest excited energy level [25,31]. The ⁴T₂g symmetry of the lowest excited state was further proved by the Zeeman splitting of the A⁺ line [28]. On the other hand, the identity of the Cr³⁺ impurity was independently stated by EPR measurements at room and low temperatures, where Gerritsen et al. [32] showed that the Cr³⁺ ions substitute for Ti⁴⁺ in the rutile lattice and found a splitting of 43.3 GHz (0.18 meV) for the ⁴A₂ ground state, also detected in the 4.2 K PL reported by Grabner et al. [25].

An example of the angular dependence of the EPR spectra taken at RT upon rotation of the LFZ grown fibres in the (001) plane is given in Fig. 5. The theoretical line positions have been calculated using the spin Hamiltonian (SH)

\[
H_{Fe} = g \beta B \cdot S + D \left( S_\perp^2 - \frac{3S}{2} \right) + E \left( S_\perp^2 - S_\parallel^2 \right) + \frac{a}{6} \left( S_\perp^4 + S_\perp^4 + S_\parallel^2 - \frac{707}{16} \right) + \frac{7}{36} F \left( S_\perp^4 - \frac{95}{14} S_\perp^2 + \frac{81}{16} \right) + C \left[ \left( \frac{7S_\perp^2 - \frac{35}{4} \right) (S_\perp^2 - S_\parallel^2) + (S_\perp^2 - S_\parallel^2) \left( \frac{7S_\perp^2 - \frac{35}{4} \right) \right] \] (1)

for the Fe³⁺ ions with S = S/2 and respective parameters given in Ref. [33], and the SH

\[
H_{Cr} = g \beta B \cdot S + D \left( S_\perp^2 - \frac{1}{3} S(S+1) \right) + E \left( S_\perp^2 - S_\parallel^2 \right) \] (2)

for the Cr³⁺ ions with S = 3/2 and respective parameters given in Ref. [32].

The spectra of Cr³⁺ and Fe³⁺ ions substituting for Ti⁴⁺ have been clearly observed (Fig. 5) indicating that both transition metal ions are present in the fibres. As can be seen in the figure, there are also spectra with deviating angular dependence, which occurs due to the presence of crystal blocks with a different orientation of the axes.

Preliminary EPR measurements at liquid helium temperatures (not shown) revealed the presence of an intense C-line (ascribed to the Ti³⁺ ions [34]), along with other defect-related spectra.

In order to correlate the infrared emission with the Cr³⁺ impurities, fibres with different amounts of chromium were intentionally grown, and no dependence of the PL luminescence on the chromium concentration was found, in accordance with the results reported by Ghosh et al. [30]. On the other hand, it is worth mentioning that infrared luminescence has also been associated to oxygen vacancies and/or Ti³⁺ interstitials [21,26]. However, the SH parameters of the C-line are not compatible with the fine structure splitting of 0.18 meV for the ⁴A₂ ground state mentioned above. As previously discussed, the PL spectral shape and temperature behaviour suggests that a transition metal ion is involved in the luminescence. From the above statements and EPR analysis, a likely candidate responsible for the optical active defect is the Fe³⁺ ion in the Ti⁴⁺ substitutional position. Indeed, the zero-field splitting for the Fe³⁺ ions, 2√D² + 3E² = 41.4 GHz = 0.17 eV, deduced from the EPR [33] is pretty close to the value of 0.18 eV obtained in the PL measurements. Nevertheless, at this stage we cannot exclude other possibilities which include other kind of defects such as, e.g., exci- toplexes bound to transition metal ions and even complex defects which involve the oxygen vacancies.

4. Conclusions

TiO₂ crystalline fibres grown by the LFZ technique were analysed by structural, optical and magnetic resonance techniques. The fibres crystallized in the rutile form contain a dominant optically active centre in the near-infrared region independently of the used pulling rates. The richly structured luminescence is characterized by the presence of two zero-phonon lines at low temperatures followed by a pronounced phonon sideband as expected for an intronic recombination of a transition metal ion. With increasing temperature, thermalization between the two emitting levels separated by ~5.0 meV was found, as evidenced by the Arrhenius plot. Angular dependent EPR measurements revealed the presence of Fe³⁺ and Cr³⁺ substitutional impurities as sample contaminants. Also, Ti³⁺ interstitials and other defects appear in the EPR spectra recorded at cryogenic temperatures. The absence of the zero-field splitting in the EPR spectra of the Ti³⁺ interstitials allows us to exclude this ion as responsible for the structured near-infrared luminescence. Additionally, no correlation of the PL intensity with the chromium concentration was found, suggesting that iron ions may be associated with the observed emission. However, at this stage, other possibilities, as, e.g., complex defects, cannot be discarded as the origin of the structured near-infrared luminescence.

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