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## Photoluminescence of synthetic titanite-group pigments: A rare quenching effect

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### ABSTRACT

Chromium-doped titanite and malayaite samples, which were synthesised to evaluate their performance as ceramic pigments, show remarkable photoluminescence behaviour. Emissions of centres related to traces of trivalent rare-earth elements (REE) are observed exclusively from chromium-free samples. Their Cr-doped analogues (containing the same REEs on the same concentration levels), in contrast, only show broad-band Cr<sup>3+</sup> emission whereas all REE emissions are suppressed. This behaviour is assigned to quenching of REE emissions by chromium centres (i.e., REE<sup>3+</sup> → Cr<sup>3+</sup> energy transfer).

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### 1. Introduction

Minerals of the titanite group (general formula CaX[O/SiO<sub>4</sub>], with X=Ti, Sn, V; space group C2/c) have been studied extensively. Whilst titanite (CaTi[O/SiO<sub>4</sub>]; Speer and Gibbs, 1976) is an ubiquitous accessory component in many igneous and metamorphic rocks, the tin silicate malayaite (CaSn[O/SiO<sub>4</sub>]; Alexander and Flinter, 1965) occurs less commonly, typically in skarns (Higgins and Ribbe, 1977). The third group-member known to date is the rare mineral vanadomalayaite (Basso et al., 1994). Takenouchi (1971) has shown that at high temperatures there exists a complete solid solution between titanite and malayaite. Both of the two minerals are characterised by an excellent thermal stability and chemical resistance. For these reasons, and stimulated by their ability to incorporate a wide range of non-formula elements in their crystal lattices, synthetic analogues of titanite-group minerals have been proposed as potential host materials for the immobilisation of radioactive waste from nuclear power stations (Lutze and Ewing, 1988).

Both titanite and malayaite are colourless if chemically pure, however they become coloured when being doped with transition

metal ions, which then act as chromophores. Especially Cr-doped malayaite, due to its intense colouration, is used commonly as a pink ceramic pigment. Correspondingly, there are many papers addressing in detail the absorption of chromium and other chromophores in titanite-group minerals, and the use of these phases as thermally stable pigments (e.g., Stefani et al., 1997; Bartis et al., 2007; Hajjaji et al., 2010; Borcanescu et al., 2013). The luminescence of titanite-group minerals, in contrast, has been investigated in very few studies only, even though “titanite may be a very interesting luminescent material” (Gaft et al., 2005). Undoped titanite shows weak green luminescence (broad band with maximum at 520 nm wavelength) under ultraviolet (UV) excitation, which is assigned to the “intrinsic” emission of TiO<sub>6</sub> polyhedrons (Blasse et al., 1988). A similar, Ti<sup>4+</sup>-related broad-band emission was observed from synthetic, Ti-activated malayaite (CaSn<sub>0.97</sub>Ti<sub>0.03</sub>SiO<sub>5</sub>; Abe et al., 2010). The emission of natural titanite, in contrast, may in some cases be most complex, comprising numerous narrow and broad bands assigned to rare-earth elements (REE, including Sm<sup>3+</sup>, Eu<sup>3+</sup>, Pr<sup>3+</sup>, Nd<sup>3+</sup>, Tm<sup>3+</sup>, Er<sup>3+</sup>) and transition metals (especially Cr<sup>3+</sup>; Gaft et al., 2003; Kennedy et al., 2010).

During a recent research project addressing oxidation states and lattice sites of chromophore ions in such titanite-group pigments, which was conducted at University Jaume I, Castellón de la Plana, Spain, several suites of titanite and malayaite samples with different levels of Cr-doping were produced and characterised

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in detail (see [Stoyanova Lyubenova et al., 2008, 2009a,b](#); [Cruciani et al., 2009](#)). In the course of a systematic spectroscopy study of these pigments that involved optical absorption, vibrational, and emission spectroscopy, we made the puzzling observation that only Cr-free samples always show emissions of minute levels of pollutant REEs. In Cr-doped samples, by contrast, REE emissions are virtually absent. In the present study we have studied the apparently unusual behaviour for REE centres in titanite-group minerals.

## 2. Samples and experimental

### 2.1. Synthesis and preparation of samples

The Cr-doped titanite and malayaite pigments and their undoped analogues were prepared by traditional ceramic method (i.e., solid-state reaction of oxide precursors). The raw materials were mixed and homogenised with water by stirring. The powders were then dried ( $100 \pm 5^\circ\text{C}$ ) and further calcined at 1200, 1300 and  $1400^\circ\text{C}$  (heating rate of  $3^\circ/\text{min}$ , and 4 h soaking time) in mullite crucibles. More details are described elsewhere ([Stoyanova Lyubenova et al., 2009a,b](#)); for generalities of the ceramics-type synthesis technique see [Cordoncillo et al. \(1998\)](#).

To eliminate the hypothetical possibility that the observed emission behaviour of trace REEs is an artefact caused by peculiarities of the ceramic-type pigment-synthesis process, additional flux syntheses of titanite samples (doped with Nd, and with and without Cr) were done. These samples were grown in a sodium-tetraborate flux (duration 10 days, peak temperature  $1130^\circ\text{C}$ ). The experiments corresponded mainly to the procedure described by [Mazdab \(2009\)](#); however we used a starting material with 1:1 molar ratio of CaO and  $\text{TiO}_2$  (with excess of  $\text{SiO}_2$ ). To extract titanite from the crucible, remnants of the flux were dissolved using  $\text{HNO}_3$  (30 wt%).

For X-ray fluorescence (XRF) analysis, pigment samples were ground in a tungsten carbide mill for  $2 \times 30$  s, to produce fine powders. The sample material was mixed with wax as a binder (1:10) and then pressed (with 150 kN for 10 s) in an aluminium cup on a layer of boric acid as stabilising substrate. For laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) analysis, pigment samples were finely powered and homogenised with a pestle in a mortar under ethanol. After drying, the samples were mixed up with “White neutral pH adhesive” (Linco, University Products, Inc.). After mixing, the samples were dried in air for several hours, cut into squares (ca.  $5 \text{ mm} \times 5 \text{ mm}$ ) and then mounted on double-sided tape. The adhesive used is extremely pure and introduces essentially no chemical impurities to the LA-ICP-MS measurements. The only impurity elements that were detected in concentrations greater than  $1 \mu\text{g/g}$  were Si ( $10 \mu\text{g/g}$ ), P ( $2 \mu\text{g/g}$ ), and Ca ( $37 \mu\text{g/g}$ ) from an average of 10 analyses of the adhesive. For back-scattered electrons imaging, samples were embedded in araldite epoxy and ground and polished; these sample mounts were also used for Raman spectroscopy. Unprepared samples were used for optical absorption and emission spectroscopy.

### 2.2. Analytical techniques

The major-element composition of pigment samples was determined, rather semi-quantitatively, by XRF analysis and X-ray diffraction (XRD) refinement. The XRF analyses were done by means of a Bruker S4 Pioneer dispersive XRF spectrometer operated at 60 kV and 66 mA. A LiF analyser and the standardless MultiRes programme were used. For XRD details, the reader is referred to [Cruciani et al. \(2009\)](#) and [Stoyanova Lyubenova et al. \(2009a\)](#).

The low levels of trace-REEs in the pigments were measured by LA-ICP-MS analysis. A Finnigan Element XR, high resolution double focusing magnetic sector ICP-MS, coupled to a Geolas 193 nm Excimer laser system, was used. The ablated material was transported to the ICP-MS using He gas with a flow rate of 1.25 l/min, with additional argon make-up gas added after the ablation cell. Laser spot sizes of  $40 \mu\text{m}$  (reference materials) and  $59 \mu\text{m}$  (ceramics) were used. The energy density was ca.  $5 \text{ J/cm}^2$  with a laser repetition rate of  $8 \text{ s}^{-1}$ . Time resolved intensity data were acquired by peak-jumping in a combination of pulse-counting and analogue modes, depending on signal strength, with one point measured per peak. The average values for CaO determined by the XRF analyses were used as an internal standard to normalise counts to concentrations. Elements in high abundance were analysed in analogue mode, whereas true trace elements were analysed using digital pulse counting mode. For external independent reference materials, NIST 610 and NIST 612 glasses ([Pearce et al., 1997](#)) and USGS standard BCR-2G ([Jochum et al., 2005](#)) were used for calibration. Data were reduced using the Iolite software package ([Paton et al., 2011](#)). For more experimental details on the LA-ICP-MS trace-element analysis routine at the Department of Earth Sciences, Memorial University of Newfoundland, the reader is referred to [Dorais and Tubrett \(2008\)](#) and [Rodríguez et al. \(2011\)](#).

Diffuse reflectance spectra of the titanite pigment samples were measured at room temperature in the spectral range  $26,000\text{--}6000 \text{ cm}^{-1}$  on a Bruker IFS66v/S Fourier-transform infrared (FTIR) spectrometer using a Perkin-Elmer diffuse reflectance accessory unit. A tungsten light source, a quartz beam-splitter, and silicon ( $26,000\text{--}10,000 \text{ cm}^{-1}$ ) and germanium detectors ( $10,000\text{--}6000 \text{ cm}^{-1}$ ), respectively, were used to cover the desired spectral range. Standard spectra were obtained from MgO powder. Standard and sample spectra were each averaged from 512 scans. The spectral resolution was  $10 \text{ cm}^{-1}$  for both detector setups. Sub-spectra were aligned in absorbance for perfect match, if necessary.

Steady-state photoluminescence (PL) spectra in the visible and near-infrared range (i.e., spectral range  $21,000\text{--}10,600 \text{ cm}^{-1}$ ) were obtained by means of two dispersive spectrometer systems. First, spectra with 488 nm  $\text{Ar}^+$  excitation (8 mW at the sample surface) were recorded using a Renishaw RM1000 system equipped with Leica DMLM microscope and a diffraction grating with 1200 grooves/mm in the optical pathway. Second, a Horiba Jobin Yvon LabRam-HR spectrometer with Olympus BX41 optical microscope and a diffraction grating with 1800 grooves/mm, was used to record PL spectra excited with the 473 nm emission of a diode laser (3 mW). Both systems were equipped with Si-based, Peltier-cooled charge-coupled device (CCD) detector. A  $50\times$  objective ( $\text{NA}=0.55$ ) was used in both cases. Spectra were calibrated using emission lines of a neon lamp. The wavenumber accuracy was better than  $0.5 \text{ cm}^{-1}$ , and the spectral resolution was determined at  $\sim 3\text{--}4 \text{ cm}^{-1}$  (RM1000) and better than  $1 \text{ cm}^{-1}$  (LabRam-HR), respectively. The latter system was used also to obtain Raman spectra for phase identification.

Time-resolved PL spectra were obtained with pulsed laser excitation (second harmonic of a Nd:YAG laser at 532 nm wavelength; pulse durations 5–10 ns). Spectra were obtained in  $90^\circ$  geometry, by means of an intensified Andor iStar CCD detector synchronised to the laser pulses. The setup used enabled us to perform measurements in selectable “time windows” that are determined by the delay time  $D$  (time period between the end of the laser pulse and the beginning of the measurement) and the gate width  $G$  (duration between beginning and end of the measurement). With a diffraction grating with 600 grooves/mm in the beam path, the spectral resolution was on the order of  $8\text{--}10 \text{ cm}^{-1}$  (or ca. 0.4 nm wavelength) in the red range.

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