

Luminescence of synthetic titanite-group pigments: A rare quenching effect

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Titanite-structured minerals are studied extensively, amongst others because of their ability to incorporate significant amounts of non-formula elements. Potential applications include their use for the immobilisation of spent nuclear fuel (Lutze and Ewing 1988) and as thermally stable pigments, for instance in tiles and domestic pottery (Stoyanova Lyubenova et al. 2008; Cruciani et al. 2009).

We have studied chromium-doped titanite and malayaite samples that were synthesised to evaluate their performance as ceramic pigments (Stoyanova Lyubenova et al. 2009), in comparison to their chromium-free analogues. We found that both materials show the same, remarkable photoluminescence behaviour. Emissions of centres related to traces of trivalent rare-earth elements (REE) are only observed for chromium-free samples. The group of narrow bands between 600 and 660 nm wavelength is mainly due to Sm^{3+} and Er^{3+} (perhaps also Pr^{3+}), and the group of bands above 840 nm is due to Nd^{3+} (Gaft et al. 2003). The Cr-doped samples, in contrast, show only broad-band Cr^{3+} emission whereas REE lines are not observed (Figs. 1, 2). There are two possible explanations: First, the presence of Cr in

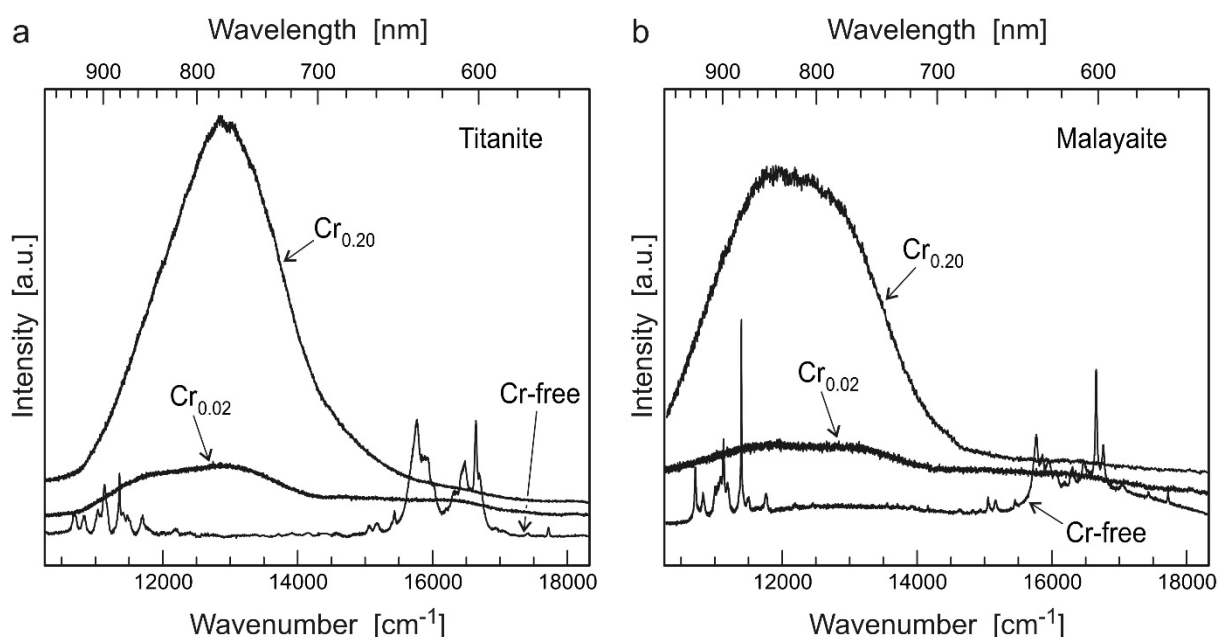


Fig. 1. Steady-state PL spectra (Ar^+ 488 nm excitation; **a**, titanite samples; **b**, malayaite samples) showing how the chromium concentration controls the presence or absence of REE-related emissions.

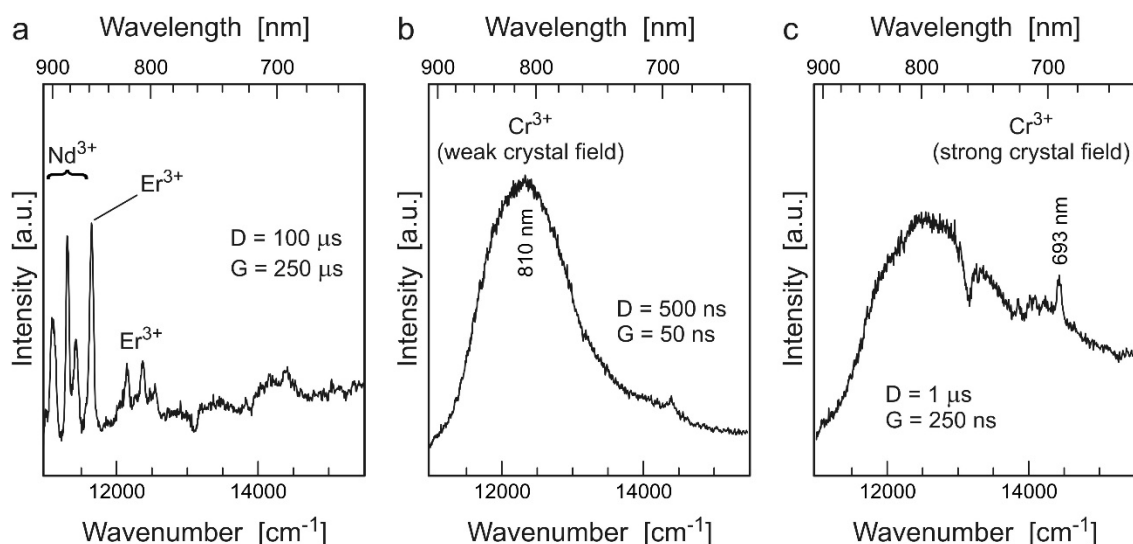


Fig. 2. Time-resolved PL spectra in the red and near-infrared region (532 nm excitation). **a** Undoped titanite showing narrow REE-related bands. **b,c** Cr-rich titanite (sample Cr0.20). There are two chromium-related emissions with different spectral positions and decay-times.

the crucible could exclude the incorporation of trace-REEs (the absence of REE lines would then be due to the absence of REE centres); second, the presence of Cr in the lattice could suppress REE emissions. The former hypothesis can be excluded, as more or less uniform REE contents were measured by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) analyses (Table 1). We assign the observed emission behaviour (Figs. 1, 2) to quenching of REE³⁺ emissions by Cr³⁺ centres (compare Reisfeld and Jørgensen 1977).

Table 1. Results of LA-ICP-MS analyses (means of multiple measurements).

Sample	Cr (wt%)	Pr (ppm)	Nd (ppm)	Sm (ppm)	Eu (ppm)	Er (ppm)
Malayaite (Cr _{0.00})	0.003	0.6	18.8	0.4	0.1	0.2
Malayaite (Cr _{0.02})	0.52	0.5	13.9	0.5	0.1	0.3
Malayaite (Cr _{0.20})	2.10	0.3	7.4	0.1	0.5	0.2
Titanite (Cr _{0.00})	0.001	0.9	5.7	0.8	0.1	0.4
Titanite (Cr _{0.02})	0.54	0.9	8.6	0.8	0.4	0.4
Titanite (Cr _{0.20})	4.24	0.7	4.1	0.5	0.2	0.3

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