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Philippe Boutinaud



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Spectroscopic investigations of calcium fluoroapatites doped with Bi<sup>3+</sup>

Philippe Boutinaud

Clermont Université Auvergne, SIGMA Clermont, Institut de Chimie de Clermont-Ferrand, BP

10448, 63000 Clermont-Ferrand, France

philippe.boutinaud@sigma-clermont.fr

## Abstract:

The spectral and dynamical properties of Bi<sup>3+</sup> in the calcium fluorophosphates Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>F and Ca<sub>5</sub>(VO<sub>4</sub>)<sub>3</sub>F are investigated at room and liquid nitrogen temperature. The data are interpreted at the light of recent semi-empirical models that allow calculating the energy of A-like (isolated Bi<sup>3+</sup>), D-like (metal-metal charge transfer) and pair-like transitions from the knowledge of the crystal structure of the host lattices. It is concluded that the attribution of the luminescence features to isolated Bi<sup>3+</sup> ions is not always an obvious option and that the luminescence can also be very satisfactorily interpreted in terms of charge transfer processes, either within Bi<sup>3+</sup>-Bi<sup>3+</sup> pairs in Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>F-Bi<sup>3+</sup> or within Bi<sup>3+</sup>-Bi<sup>3+</sup> and Bi<sup>3+</sup>-V<sup>5+</sup> pairs in the newly reported Ca<sub>5</sub>(VO<sub>4</sub>)<sub>3</sub>F-Bi<sup>3+</sup>.

## Keywords:

Bi<sup>3+</sup>, charge transfer, luminescence, pairs

## 1. Introduction

Although investigated for decades, the spectroscopy of trivalent bismuth in solids is still not totally fixed. The reason is that the emission of this ion can arise from different kinds of excited states: "regular" states belonging to isolated Bi<sup>3+</sup> ions or states with charge transfer character, including Bi<sup>3+</sup> pairs. Depending on the doping rate, on the nature of the host lattice and on external stresses like temperature or pressure, more than one emission process can occur [1-4]. This concomitancy usually generates complex spectra and is the origin of many controversies in terms of spectral assignments. As a case study, the luminescence properties

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