X-ray Natural Linear Dichroism: The case of alexandrite $BeAl_2O_4:Cr^{3+}$

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In this study we investigated the electronic structure and local environment of Cr^{3+} in alexandrite $BeAl_2O_4:Cr^{3+}$ using a theory-experiment coupling of X-ray absorption spectroscopy (XAS). The features in *K*-edge X-ray absorption spectra of transition metal cations provide information about their crystallographic environment and electronic structure in minerals. Fine details can be revealed from the pre-edge and edge features by performing measurements for different orientations of a single-crystal with respect to the polarization of the incident X-rays beam (Brouder 1990).

Alexandrite is a chrysoberyl containing chromium as an impurity. Since alexandrite crystallizes in the *Pnma* orthorhombic space-group, it appears to be a trichroic crystal for what concerns XAS: the Cr *K*-edge spectrum will be different for three orthogonal orientations of the crystal with respect to the incident beam. The single-crystal investigated here comes from Kilombo of the Nova Era district in the Minas Gerais state (Brazil) and contains ca. 4410 ppm Cr_2O_3. Its corresponding formula is $Be(Al_{1,976}Ti_{0,007}Cr_{0,008}Fe_{0,009})O_4$.
We recorded the Cr *K*-edge X-ray absorption spectra on the SuperXAS beamline at the Swiss Light Source (Villigen, Switzerland). In a first set of measurements, spectra were recorded on a single-crystal with the polarization of the beam parallel to the (i) **a** axis of the crystal, (ii) **b** axis and (iii) **c** axis. The XNLD signal is very well observed: we have three very different spectra in the three directions. In a second time, we have recorded the XANES spectrum for a powder sample to get the isotropic signal. A very good agreement is obtained between this isotropic signal and the one reconstructed from the oriented spectra (Brouder 1990).
To better understand the experimental spectra, we performed *ab initio* calculations based on the Density Functional Theory. Indeed the comparison between experimental and calculated data makes it possible to obtain accurate information about the crystallographic and electronic structures of transition metals in minerals. It provides quantitative information about the relaxation of the crystal structure around the impurity, which a key parameter for understanding the mechanisms controlling the incorporation of colouring impurities in minerals. We determined with the Quantum-Espresso suite of codes (Giannozzi et al. 2009) the spectra for the three orientations and the reconstructed isotropic signal. A good agreement was obtained between experiments and theory.

This coupled approach of theory and experiments was already successfully used to investigate impurities in dichroic crystals, e.g. V^{3+} in garnet (Bordage *et al*. 2010). Nevertheless this new work demonstrates here the applicability of this approach to more complex minerals, such as trichroic crystals, which have not been very much studied by XAS. These new results on Cr^{3+} in alexandrite will also contribute to better understand the incorporation of Cr and Fe in chrysoberyl $BeAl_2O_4$.

References:
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