

Combined IonoLuminescence and PIXE micro-analyses of natural diopside for activators and quenchers identification

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Diopside is a mineral belonging to the pyroxene group, a single chain inosilicate with chemical formula $CaMgSi_2O_6$, occurring mostly in basic and ultrabasic igneous rocks or in metamorphic rocks. Natural diopside displays a large variety of luminescence centers: main features at room temperature are an intense band around 585 nm that can be ascribed to Mn^{2+} ions in M2 (Ca^{2+}) sites¹ and a 430 nm band, attributable to the silicate-based network^{2,3}. Also, Ti³⁺ and Fe-related impurities have a role as activators of luminescence⁴.

The presented study is part of a huge characterisation project of lapis lazuli of historical and archaeological interest, hence a hundred of diopside crystals selected in lapis lazuli samples of different provenances (Afghanistan, Tajikistan and Siberia) have been investigated. Micro-beam PIXE (Particle Induced X-ray Emission) and IL (IonoLuminescence) have been simultaneously performed at the INFN-LNL (Legnaro National Laboratories of the Italian National Institute of Nuclear Physics) with a 2 MeV proton microbeam provided by a Van de Graaff accelerator.

The great amount of data collected during these irradiation sessions has already been used to extrapolate relevant information for lapis lazuli provenance determination⁵. In addition, we have also been able to investigate the correlations between some features of the ionoluminescence behaviour and elements detected in traces as possible activators. For example, while the 585 nm band resulted in a strong signal for Afghanistan and Tajikistan samples, it was almost undetectable in samples from Siberia (fig.1a). These latter samples have also a much higher iron content: we found out that the intensities of the IL peak are in a good linear correlation with concentrations of Mn in the crystal, once the competition with the action of quenchers, such as Fe²⁺, is suitably taken into account⁶ (fig.1b). Other newly attribution in diopside are a band at 785 nm, probably due to the presence of V, and two peaks at 603 and 641 nm, correlated to Y.



Figure 1: (a) IL spectra of diopside crystals from different provenances. The 585 nm peak is highlighted. (b) Correlation of the 585 nm band intensities with Mn/Fe concentrations.

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