Study of Activators and Ion Damaging Effects in Natural Diopside by Means of Micro-Ionoluminescence and Micro-PIXE

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INTRODUCTION

Diopside is a mineral belonging to the pyroxene family, in particular it is an inosilicate with a single calcium and magnesium chain, whose chemical formula is $CaMgSi_2O_6$. Natural diopside displays a large variety of luminescence centers: at room temperature main features are a 450 nm band, that can be ascribed to the silicate-based network [1-3] and an intense band at 585 nm that can be ascribed to Mn^{2+} ions in M2 (Ca^{2+}) sites [4]. Also Ti^{3+} and Fe-related impurities have a role as activators of luminescence [5,6].

The main purpose of the present work is to study the radiation hardness of several of such centers by following the evolution of ionoluminescence upon proton irradiation. Moreover an attempt was made to correlate the trace elements to the centers of luminescence by means of micro-PIXE.

EXPERIMENTAL

As this work falls in the framework of the provenance study of lapis lazuli used for artworks we are carrying on since 2008 [7], all analysed natural diopside crystals were found in lapis lazuli rocks: some of them belong to the collection of the Mineralogy and Lithology section of the Museum of Natural History, University of Firenze and others bought at the Turin International Mineral Show since 2010. They are 4 samples, 3 from Afghanistan and 1 from Pamir and they were prepared as semi-thin sections (about 80 µm thick). In these samples 17 diopside crystals have been selected on the basis of their homogeneity (evaluated by means of cathodoluminescence imaging).

These crystals have been analysed by means of micro-Ionoluminescence and micro-PIXE at the same time using 2 MeV proton-beam at the AN2000 microbeam facility. The beam was focused to a spot size of ~5 µm and raster-scanned over the samples.

The Ionoluminescence spectra have been acquired through a lens connected to an Ocean Optics spectrometer with an optical fiber. For PIXE measurements, to simultaneously analyze light and heavy elements with the same detector, we used an aluminum funny filter, that is a filter with a hole drilled at its centre and placed in front of the detector window. A set of reference mineral standards has been acquired and spectra analysis has been carried out through the Gupixwin software. To test the validity of the quantification a standard of diopside has been analyzed.

RESULTS AND DISCUSSION

All the acquired luminescence spectra show the typical features of the diopside luminescence (figure 1): a large band at around 450 nm due to the silicate-based network and an intense band at 585 nm due to the presence of Mn. Moreover some other bands have been detected but only in some samples: in two of the three afghan samples a large band is present, centered at about 780 nm (figure 1a). In the third afghan sample more features are present: a band in the ultraviolet region, two narrower peaks at 600 and 650 nm and a series of peaks after 850 nm (figure 1b). Finally, in the sample from Pamir, a band centered at 700 nm is present (figure 1c).

Since the luminescence band at 585 nm is present in all the analyzed crystals, the correlation between its intensity and the manganese concentration have been evaluated: as expected, when the activator concentration increases, also the luminescence intensity of the band at 585 nm increases (figure 1d).

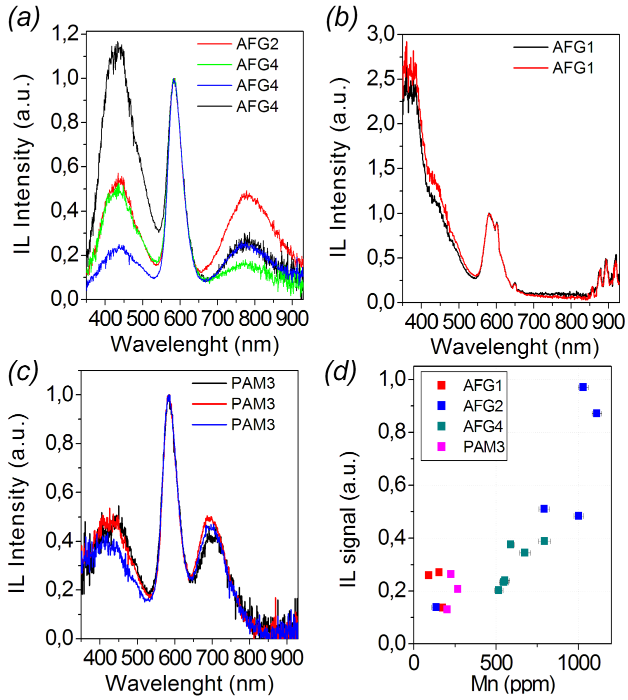

Fig. 1. (a,b,c): ionoluminescence spectra of diopside crystals inside lapis lazuli samples; spectra are corrected for detector efficiency and normalized at the height of the band at 585 nm. (d): correlation between the luminescence intensity of the band at 585 nm and the Mn concentration.

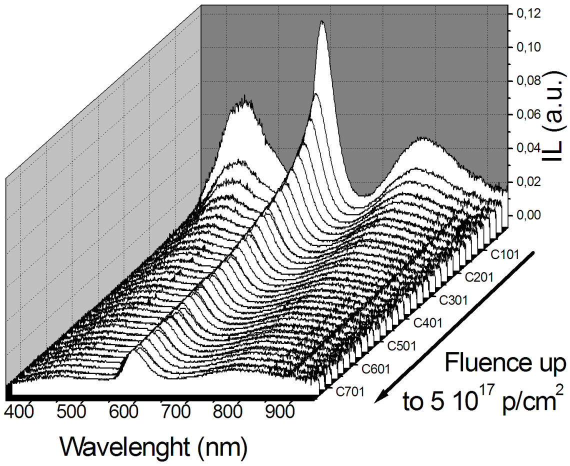

Fig. 2. Evolution of ionoluminescence spectrum of a diopside cristal during ion damaging with a 2 MeV proton beam.

To evaluate the correlation of other luminescence bands with other element concentrations a higher number of crystals have to be analyzed.

Another aspect that have been evaluated is the radiation hardness of the different luminescence bands in diopside: a selected crystal from an afghan sample have been hit with a 2 MeV proton beam up to a fluence of $5 \cdot 10^{17}$ p/cm^2. As can be seen from figure 2, during the damage all the luminescence bands decrease their intensity, but with different rates: both the band at 450 nm and at 800 nm decrease quite rapidly increasing the fluence, while the band at 585 nm persists, even if considerably reduced, up to a high fluence ($5 \cdot 10^{17}$ p/cm^2), showing to be the band with the higher radiation hardness in diopside. The luminescence intensity of this band halves after $5 \cdot 10^{16}$ p/cm^2.

It is worth to stress that none of these measurements changes the external aspect of the crystals, allowing to analyze artworks or precious materials containing diopside.

CONCLUSIONS

The trace elements in diopside crystals and their luminescence emission have been contemporarily evaluated by means of micro-PIXE and micro-IL. A first attempt to correlate some of the luminescence bands to a specific activator has been done: the band at 585 nm has been confirmed to be due to Mn presence, while to try an attribution of the other bands more statistics is required.

Moreover the radiation hardness of several of such centers have been studied following the evolution of ionoluminescence upon proton irradiation: the band at 585 nm demonstrated to have a higher radiation hardness than the other bands.

Further studies will allow to better describe the radiation hardness of all the luminescence centers changing both the particle probe (proton or helium) and its energy.

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