Study of luminescence properties in lapis lazuli diopside crystals during micro-IBIL measurements

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INTRODUCTION

Micro-Ion Beam Induced Luminescence or micro-IBIL consists of the photon emission in the IR-VIS-UV range from a crystalline material that occurs when a significant amount of energy is transferred to it by an ion probe. The intensity and wavelength of the luminescent light provide information on the nature of luminescence centers, such as trace-level impurity interstitial and structural defects of the matrix. In the framework of the Ion Beam Analysis applied to cultural heritage studies [1], IBIL is usually acquired simultaneously with other complementary techniques, such as PIXE, generally guaranteeing a completely non-destructive approach, which is suitable in the case of archaeological or artistic samples. However, the interaction of the proton beam with the atoms of the target crystal, with the possible creation of local radiation-induced structural damages, can affect the luminescence response and so the detection of a signal useful for analysis. In the present work, a preliminary investigation of the radiation hardness of a reference diopside crystal ($CaMgSi_2O_6$) inside a lapis lazuli rock is presented. This is realized by following the evolution of its IBIL signal upon proton irradiation and by comparing the results obtained repeating the same measurement after 2 years with the same experimental setup. This work falls in the framework of the provenance study of lapis lazuli that the Solid State Group of the University of Torino is carrying on since 2008 [2]; in the provenance study, the position of the luminescence bands of diopside crystals represents a useful marker for distinguishing among different sources of the raw rock used for lapis lazuli artworks in antiquity.

EXPERIMENTAL

The diopside crystal chosen as reference target belongs to an Afghan lapis lazuli rock sample prepared as semi-thin petrographic sections ($\sim$100 µm thick); the crystal was selected for its homogeneity and its easy identification on the sample. Fig.1 shows the target crystal and the surrounding area in the visible and SEM-BSE images, together with Ca, Si and Mg PIXE maps acquired on the crystal. IBIL analysis has been performed by using a 2 MeV proton beam at the AN2000 microbeam facility. The beam was focused to a spot size of $\sim$5 µm and raster-scanned over a 30×30 µm^2

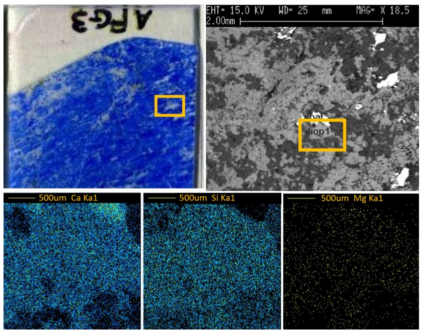

Fig. 1. (Up) Petrographic section of the rock sample (left) and SEM-BSE (right) image acquired in the area of the target diopside crystal and highlighted by the yellow box. (Down) PIXE maps of Ca, Si and Mg acquired on the crystal.

area inside the diopside crystal. The IBIL spectra have been acquired through a collecting lens, positioned inside the vacuum chamber with an angle of 45° with respect to the beam direction, and connected with an optical fiber to an Ocean Optics USB4000 spectrometer (3648 pixels, fitted with a 600 l/mm grating blazed at 500 nm). The whole system has a sensitive bandwidth of 350-900 nm. The integration time for each acquired spectra is 10 s and the total acquisition time for the test was of about 4 minutes. In order to test the possibility of re-analyzing the same crystal after a proton beam irradiation and verify that the fluence usually selected for the lapis lazuli provenance investigation does not severely compromise the luminescence of target crystal, another measurement with the same experimental configuration was repeated after 2 years. However, since the exact same condition of beam current as well as the angle position and distance of the collecting lens of µ-IBIL is difficult to replicate at a micrometric scale (the set-up is installed and removed in the chamber at every measurement runs), only qualitative comparison among the intensities of spectra acquired in different measuring runs can be performed. Diopside3

RESULTS AND DISCUSSION

All the acquired IBIL spectra show the typical features of the diopside luminescence in Afghan rock samples: 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.

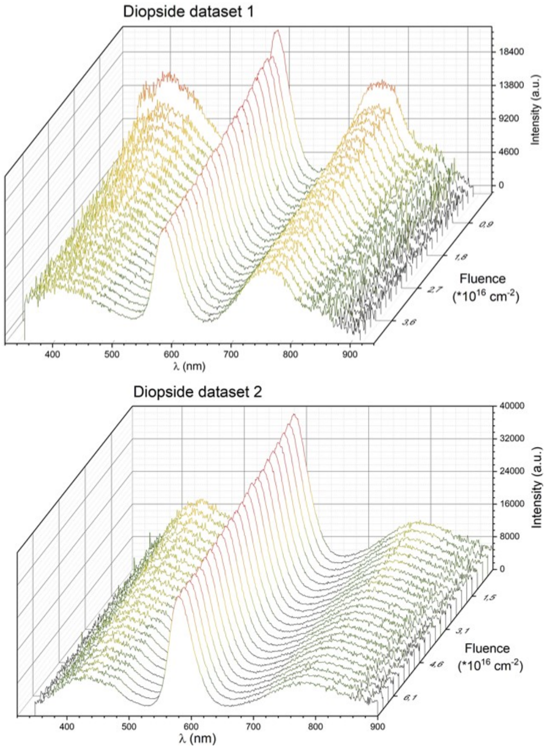

Fig. 2. Evolution of IBIL spectrum of the diopside crystal as a function of the fluence for the two datasets.

A broad third band, around 740-780 nm, is also present, probably due to Cr and Fe-related impurities [3]-[4]. Fig.2 shows the evolution of the IBIL spectrum in dataset 1 and dataset 2 (acquired 2 years later) emitted by the same diopside crystal during the proton beam irradiation for the same amount of time. All the spectra were corrected for the efficiency of the spectrometer. It is important to notice that in the IBIL spectra of the second measurement run all the luminescence bands useful for the provenance studies are still clearly visible, proving that the beam irradiation in the previous run has not critically compromised the crystal luminescence features. Preliminary results also show that during the irradiation the intensity of all the luminescence bands decrease, but with different rates. This can be seen also in Fig.3, where the peak intensity of the three main bands is reported as a function of the fluence for the two datasets. Fitting each curve with a simple exponential model and comparing the decay constant parameters obtained (Fig.4), one can obtain a roughly evaluation of the radiation hardness of the bands; in both datasets the band at 400-450 nm is the most affected by the radiation damages induced by the proton beam, whereas the 740-780 nm band shows the highest radiation hardness.

CONCLUSIONS

The comparison between the μ-IBIL spectra of the same diopside crystal acquired in two measurement sessions at the AN2000 microbeam line at two years of distance has been presented. Preliminary results show the possibility of re-analyzing the same crystal after a proton beam irradiation since the fluence selected for the lapis lazuli provenance investigation does not severely compromise the luminescence features of the target crystal. The radiation hardness of the crystal has also been studied following the evolution of its luminescence signal during proton irradiation: the band around 760 nm demonstrated to have a higher radiation hardness than the other bands. Further test could be done in the future to better investigate the radiation hardness of the luminescence centers in lapis lazuli minerals, for example by acquiring IBIL data with a shorter time interval between the two measurement runs (e.g. days or hours), improving in this way the reproducibility of the experimental configuration, and by extending this kind of test also to other minerals considered in the lapis lazuli provenance study, such as calcite and K-feldspar.

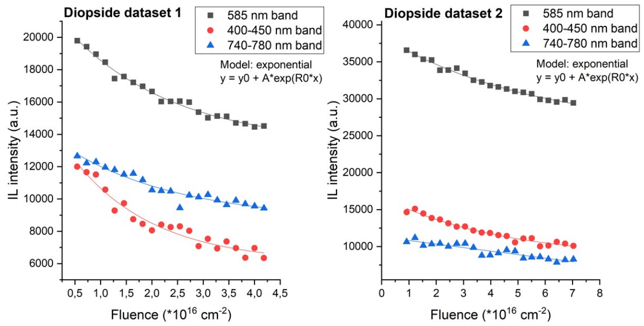

Fig. 3. Evolution of the peak intensity of the main bands in diopside spectra as a function of the fluence for the two datasets. The expression of the exponential curve used for the fitting procedure is reported.

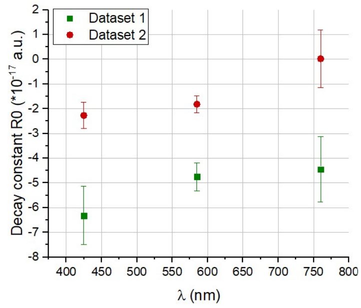

Fig. 4. Decay constant R0 parameters obtained from the exponential fit of the data shown in Fig.3 for the two datasets.

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