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ABSTRACT

This work will present preliminary results concerning the use of time-resolved ion beam induced luminescence applied to provenance studies of lapis lazuli. Measurements were performed at the pulsed beam facility at LABEC laboratory in Florence. Lapis lazuli is a semi-precious gemstone, used as ornament since the early civilizations that can be found in few places on Earth. The importance of this work lies in understanding the origin of various samples of lapis lazuli, from which it may be possible to gain insight into trade routes from ancient times. The samples studied in this work originated from Chile, Afghanistan, Tajikistan, Myanmar, and Siberia. The stones were irradiated with 3 MeV protons and the resulting luminescence was detected by a photomultiplier tube, whose output was acquired using a sampling digitizer VME module (CAEN/V1720). Wavelength discrimination was performed at 430 nm utilizing a range of beam currents. The results showed that, by changing the beam current intensity, one can study different features of lapis lazuli, and this may aid in distinguishing lapis lazuli from different provenances.

1. Introduction

When studying insulators and semiconductors, luminescence techniques can be extremely powerful as they give information about structural defects and impurity sites [1]. Among the possible excitation sources such as photons and electrons, ion beams can offer particular advantages. Ion beam induced luminescence (IL) technique [2] allows for the changing of the excitation depth profile by varying ion energy and mass. Moreover, the rate of energy deposition along the ionization track can also be changed. Although it is still not fully understood, the process behind IL can be comprehended in terms of basic notions. When an ion beam collides with a crystalline material it generates an excited lattice and excited impurities. Through different relaxation mechanisms the material can return to the ground state, with non-radiative and radiative emissions. Techniques based on luminescence detection can be very sensitive to the presence of d-transition metal ions and rare earth elements because IBIL depends on the chemical state of the emitting atom, as well as local symmetry, the covalent character of the bonds it forms, and the spatial symmetry of the crystalline lattice [3]. In fact, these techniques have been applied to the characterization of minerals with interesting results [4]. The LABEC laboratory in Florence, with a long record of cultural heritage studies [5,6] and environment [7,8], has

applied ionoluminescence spectroscopy to the provenance studies of lapis lazuli [9–14]. This very heterogeneous material has been a matter of study in several laboratories [15–19]. It consists of many minerals such as, for example, lazurite, diopside and pyrite, whose crystals have a size ranging from few micrometers to millimeters. Lapis lazuli has been traded since early civilization and can only be found in few places on Earth like Chile and Siberia. The importance of being able to characterize lapis lazuli from different origins comes with the fact that it can help in understanding different trade routes in ancient times [20]. The results from previous studies have offered a strong marker that can help distinguish Chilean lapis lazuli from other samples. Specifically, Chilean ones are characterized by a double emission band at 560 nm and 620 nm, which are due to the presence of the mineral phase wollastonite, while Asian samples are characterized by an emission at 580 nm, due to the mineral phase diopside. Additionally, samples from all origins show a band at 450 nm.

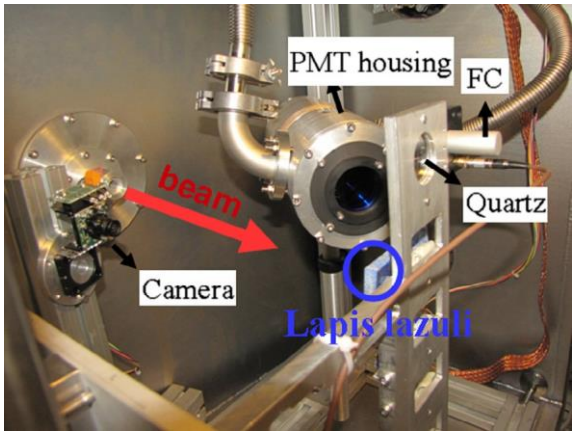

Fig. 1. Experimental setup inside the measurement chamber. The PMT was housed inside a small chamber to be placed in vacuum. It was positioned facing the lapis lazuli samples, which can be remotely placed in front of the beam by a motorized sample holder. In the figure it is also possible to see diagnostic elements: a Faraday Cup (FC), a quartz window, and a camera.

With the objective of finding new markers to distinguish lapis lazuli from different origins, we decided to perform time resolved luminescence measurements [21]. The idea behind the application of time-resolved ion beam induced luminescence (TRIBIL) [22–24] to the provenance study of lapis lazuli is that it can resolve overlapping features that would be otherwise indistinguishable using steady-state data [25]. If one considers a single luminescent center, the luminescence decay process is exponential over time. The lifetime is the time that a luminescence center spends in the excited state prior to its return to the ground. In the exponential case, this is the time that the luminescence intensity drops to 1/e of its original value. It must be kept in mind that the luminescence decay of a heterogeneous material as lapis lazuli is normally due to the simultaneous emission from many luminescence centers and mixed impurities. Furthermore, the behavior of the time-resolved decay curve depends on processes like energy transfer, sensitization, reabsorption and quenching [26]. The objective of this work is to understand the luminescence behavior of lapis lazuli. For this reason, we focused our efforts in finding a parameter that can be compared and used to distinguish the stones from several places.

2. Experimental

All TRIBIL measurements were performed at LABEC laboratory in Florence at the pulsed beam facility (DEFEL). LABEC is equipped with a 3 MV Tandetron accelerator that was used in this project to accelerate protons up to 3 MeV. The DEFEL beam line has been extensively described previously in other works [27–29]. Essentially, it consists of two electrostatic deflectors that, when working together, can produce a pulsed

beam from a continuous one. Each deflector also has the option to work independently, allowing for versatility in probing the target, like delivered dose and irradiation time [30]. The results shown below are related to measurements carried out using only one of the deflectors, which continuously irradiates the target for a short time period that can be set from 800 ns to 5 ls. To the time the measurements were performed it was not possible to acquire any luminescence signal using ion bunches of few ions and short irradiation time. Since minerals usually show long lifetime values of microseconds and milliseconds [6], the pulse duration of 800 ns used in this work not only provided high luminescence intensity but also enhanced the contributions of longer lifetime emissions to the total luminescence decay. It is worth noticing that a pulse duration of 800 ns would result in a small, if any, contribution to the total decay time, when studying slow luminescence decay. Nonetheless, we plan to modify the deflector configuration in order to be able to obtain shorter pulses but still high ionization density. In this way, we will be able to analyze also fast components of the luminescence emission of lapis lazuli.

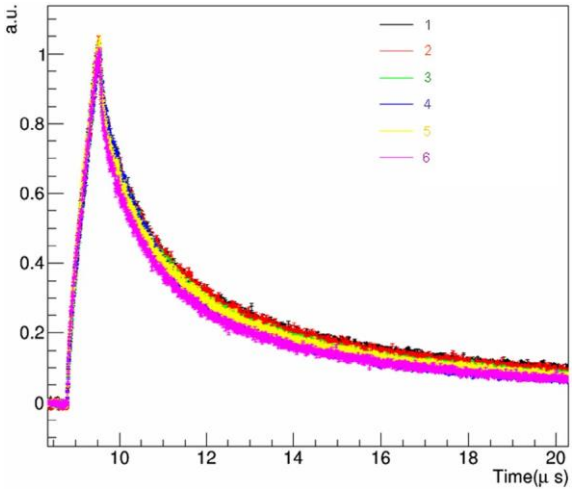

Fig. 2. Average luminescence signals of six different irradiated areas (different colors) from an Afghan lapis lazuli sample. The waveforms have been normalized to their maximum intensities. Target irradiation proceeds until the signal has increased to a maximum. After excitation has been switched off, the subsequent signal decrease corresponds to the luminescence decay. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The thirteen studied lapis lazuli samples were provided by the Museum of Natural History of Florence and by the University of Turin. Two of the samples originated from Badakhshan in Afghanistan and three from Ovalle in Chile; all these samples, which have certified origins, were acquired at the international exhibition ‘‘EuroMineralExpo – Turin”. The two samples from Mogok in Myanmar were directly obtained in place by one of the authors (A. Re.) The two stones from Liadjura-Dara in Tajikistan (Pamir Mountains) and the four from Lake Baikal area in Siberia were directly extracted in a mission financed by the Museum of Natural History of Florence. The samples were irradiated in vacuum and the luminescence signal was detected using a photomultiplier tube (PMT, Electron Tubes/9256 KB) with a spectral range between 290 and 680 nm and enhanced green sensitivity. Vacuum irradiation allowed us to use even very high beam current intensities without worrying about possible extraction window rupture. Nonetheless, in the future, with an optimized configuration, it will be also possible to exploit the provenance markers found in these conditions also in external configuration. In Fig. 1, it can be seen that to avoid problems due to power dissipation in vacuum, the PMT was housed in a vacuum-tight box, where it was cooled by a continuous blow of air at ambient temperature (two leak-tight ducts connected the PMT box to ambient pressure, in this way working temperature was maintained using a steady flux of air, without any raise of the pressure inside the vacuum chamber).
The lapis lazuli samples were placed in front of the pulsed beam on a motorized sample holder. The PMT was positioned facing the samples and optical filters were used by placing them in front of the PMT window. From

Fig. 1 it is also possible to see various positioning and diagnostic elements such as a Faraday Cup (FC) for beam current measurement, a quartz window for beam centering, and a camera for monitoring.

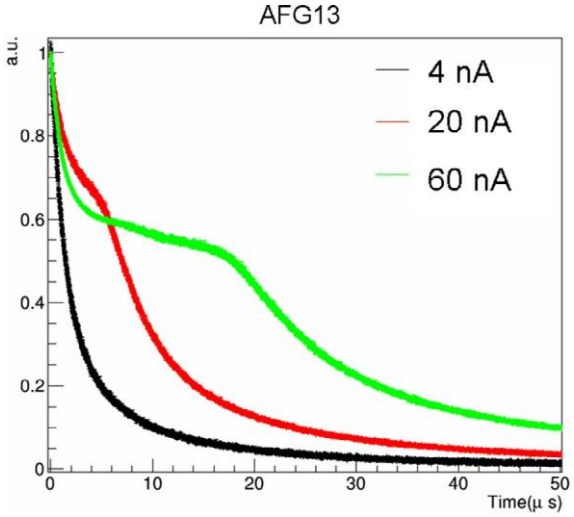

Fig. 3. Normalized luminescence decay curves of an Afghan sample acquired irradiating the same area. The curve in black corresponds to the irradiation performed with a beam current intensity of 4 nA, the red with 20 nA, and the green with 60 nA. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The PMT output was directly sent to a sampling digitizer VME module (CAEN/V1720). The external trigger used to control the signal acquisition comes from the driver of the used deflector. Each time the deflector makes its transition to ON mode, i.e., when the beam hits the target, a trigger pulse is sent to the digitizer and a predefined number of signal samples before and after the trigger are acquired. The digitizer buffer works in a circular manner so it is constantly sampling. Each time a trigger occurs it saves a predefined number of samples, already available in the buffer, before the trigger for baseline calculation, and another amount of samples after the trigger. The time window length is chosen in such a
way that it is possible to see the luminescence evolution during and after the target irradiation. The signal is analyzed until the luminescence intensity reduces down to 3r, where r represents the baseline standard deviation.

Knowing that lapis lazuli has a characteristic emission band at 450 nm, wavelength discrimination was performed by placing an optical filter in front of the PMT window (transmission band at 430 ± 50 nm). The irradiation time was set to 800 ns, the shortest possible time length for particle bunches at the DEFEL facility in the high intensity mode (about a million ions per bunch, exploiting only the first deflection stage). The trigger frequency was 5 Hz. Also, since it is known that emission centers are often sensitive to the rate of energy deposition [31], we used this parameter as a way to probe different features from lapis lazuli by changing the beam current intensity. Results reported here were obtained with beam currents of 4, 20 and 60 nA.

When irradiating the lapis lazuli samples, one is actually irradiating several minerals simultaneously. This happens because the beam spot on the target has a dimension of few millimeters and because 3 MeV protons penetrate tens of micrometers into the material [10–13], so allowing testing the bulk properties of the material. For this reason, for now, we are working with the concept of average decay time. To achieve this value, about 6 different areas across each sample were irradiated. The areas were chosen attempting to take equal numbers of blue and white regions. The decay curve obtained for each examined area represents an average of 500 digitized single decay curves. For each of these averaged decay curves the average decay time, or mean decay time, is calculated by integrating the luminescence intensity I(t) in time. This integration begins immediately following the conclusion of excitation (t_0) and continues until the luminescence intensity reduces down to 3r (r is the baseline standard deviation) at t_f. This can be seen as following:

$$\tau = \frac{\int_{t_0}^{t_f} tI(t)dt}{\int_{t_0}^{t_f} I(t)dt}$$

In the end, we obtained a final comparable value that represents the average decay time for each provenance. This was calculated by averaging the mean decay time over different areas from the same sample and also over different samples from the same origin.

3. Results and discussion

Each lapis lazuli sample was irradiated across six different areas. As an example, Fig. 2 shows the normalized luminescence decay, filtered in a 100 nm wide spectral region centered at 430 nm, for each area of an Afghan sample irradiated with 4 nA of beam current. Before the start of signal increase, there are the signal samples for the baseline calculation that in Fig. 2 was already subtracted. The start of the signal rising corresponds to the arrival of the bunch of protons on the target. The signal reaches a maximum that in this case corresponds to when the excitation is switched off and subsequently decreases. As it can be seen in Fig. 2, in this case the decays differ in some extent within the same sample, but the overall shape is similar and the curves superpose one another. In other cases the emission differs significantly from one area to another within the same sample, which results in larger uncertainties in the results presented below (see Fig. 4).

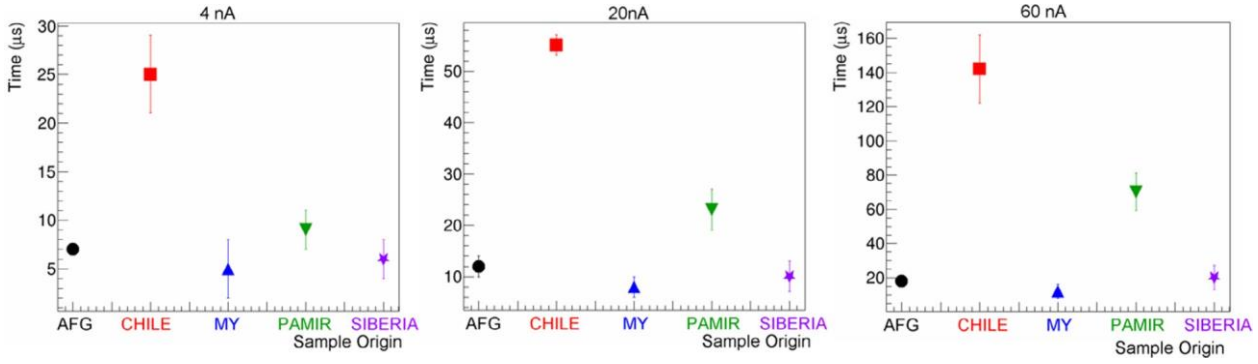

Fig. 4. Average decay times of the luminescence filtered in a 100 nm wide spectral region centered at about 430 nm, obtained for each provenance studied. In black circle are the samples from Afghanistan, red square from Chile, upward blue triangle from Myanmar, downward green triangle from Pamir (or Tajikistan) and violet star from Siberia. The first graph on the left shows the results for the irradiations with a beam current of 4 nA, the one in the middle for 20 nA and the one on the right for 60 nA. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The influence of the energy deposition rate on the excitation of different emission centers, or even on different emission processes, can be seen in Fig. 3. Here, we show the emission of the same area of one Afghan sample, irradiated for 800 ns with beam currents of 4, 20 and 60 nA. All the decay curves showed in Fig. 3 are normalized to the intensity when the excitation is switched off. In the case of the 4 nA irradiation, the particular luminescence decay can be described by a multiexponential curve. However, after increasing the beam current, different decay features became detectable, and the resulting luminescence decay dynamics could not be as easily described. Since the objective of the project is not to model the singular behavior of lapis lazuli but to compare various lapis samples from different origins, we made use of the concept of average decay time, previously described.

For the determination of the mean decay time we used luminescence curves acquired by detecting light passing through an optical filter for wavelength discrimination with the transmission band at 430 nm. The results for the mean decay time obtained for each lapis lazuli origin studied are shown in Fig. 4. Irradiating the Chilean lapis lazuli with a beam current intensity of 4 nA, a mean decay time around 3 times longer than

the others is obtained. However, it was not possible to discriminate the origin of the remaining samples with this small beam current. But, by increasing the beam current, we began to observe unique decay patterns which separated the Pamir lapis lazuli samples from those of different origins. Moreover, the difference between the Chilean samples and the ones with the lowest decay time become more evident. When irradiating with a beam current of 60 nA, Chilean lapis lazuli showed an average decay time that was seven times longer than samples from Afghanistan, Myanmar, and Siberia. Pamir samples presented a decay time that was around two times shorter than Chilean ones and three times longer than the others. However, as a general rule, it is possible to say that, to distinguish among two different origins, one has to consider the difference of the mean decay times, taking into account the uncertainty of the values. With this in mind, one has to choose the optimum irradiation condition for which the difference of the mean decay times is more statistically significant.

4. Conclusion

TRIBIL measurements were performed at LABEC laboratory for the source identification study of lapis lazuli stones. The pulsed beam facility DEFEL was used to irradiate stones of known origins with 3 MeV protons in order to test the bulk properties of the material. Lapis lazuli targets were irradiated for 800 ns with a trigger frequency of 5 Hz. We studied the time evolution of the ionoluminescence signal at a 100 nm wide spectral region centered at 430 nm, where it is known that lapis lazuli has a characteristic emission band (450 nm). By using the average lifetime, we were able to compare the results obtained by irradiating the samples with three different beam current intensities (4, 20 and 60 nA).

The preliminary results obtained and presented here show that the average decay time is different for diverse dose rates. This seems to provide an experimental procedure to identify lapis lazuli from Chile and Pamir, thus distinguishing between themselves and all the other origins.

Regarding future work, measurements with different optical filters and other wavelength ranges will be performed. In addition, modification of the deflector configuration will make it possible to perform high dose rate/high intensity measurements with shortest time duration. The DEFEL facility at LABEC, which now is also available for TRIBIL measurement, has showed its great versatility in probing a target, thus being extremely powerful in several material analysis studies.

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