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Ionoluminescence spectroscopy and microscopy of lapis lazuli

T. Nikbakht*, O. Kakuee, M. Lamehi-Rachti

Physics & Accelerators Research School, NSTRI, P O Box 14395-836, Tehran, Iran

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ABSTRACT

Natural heterogeneous lapis lazuli has been investigated using the complementary techniques of ionoluminescence spectroscopy, ionoluminescence microscopy and micro-PIXE. The equivalent probed depths, the possibility of simultaneous use and the capability of non-destructive in-air application suggest the combined use of ionoluminescence and micro-PIXE techniques as an appropriate approach in mineral analysis to reveal the texture, chemical composition, and elemental distribution of the samples. In this research work, the various mineral phases of a lapis lazuli sample were detected and analyzed. It was possible to identify most of the minerals in the analyzed area, including apatite, a mineral phase uncommon in lapis lazuli, and point out different luminescence features of crystals of the same mineral, diopside, found in different parts of the same lapis lazuli sample.

1. Introduction

The formation processes of mineral phases, regarding their different environmental conditions, result in different properties of the geological samples, which have been mainly studied by the cathodoluminescence (CL) technique. It reveals the conditions during crystal growth, the internal structures and homogeneity of the crystals, the defect density and incorporation of trace elements, including their valence, site occupancy and distribution within the sample, see e.g. [1–3]. CL, in combination with micro-PIXE, has been employed as a sensitive method to analyze geological samples [4,5]. However, the penetration depths of typical ion and electron beams, applied in micro-PIXE and CL experiments, are not of the same order; for instance, the penetration depth of 2.4 MeV proton beam in a gemstone is tens of micrometers, while the corresponding value for 15 keV electron beam is only a few micrometers [6]. Therefore, considering the possible structural and elemental changes of the samples with depth, the results of such ion and electron probes are not necessarily comparable. In this regard, the equivalent probed depths and also the possibility of simultaneous application of ionoluminescence (IL) and micro-PIXE suggest them as more suitable complementary techniques for this kind of studies. Moreover, the possibility of in-air implementation of both IL and micro-PIXE allows for non-destructive analysis of art objects and precious samples [6,7].

The combination of IL and micro-PIXE provides a sensitive method for mineral analysis [8–11]. In this regard, IL provides information about structure, chemical composition, and distribution of mineral phases of samples, while micro-PIXE determines their elemental distribution and concentrations. Despite the low detection limit of micro-PIXE [12], relatively long integration times are required for detecting trace elements in minerals. Herein, as a suitable complementary technique for micro-PIXE, IL is a relatively fast technique which is capable of detecting trace elements of minerals with very low detection limits (even below ppm) [13]. Although the combination of IL microscopy, IL spectroscopy and micro-PIXE techniques provides detailed and comprehensive information about minerals, it has been introduced quite recently for lapis lazuli characterization (see e.g. [7,9–11,14–17]).

Regarding the cultural and historical importance of the heterogeneous lapis lazuli gemstone, its investigation, especially its provenance study, has been a subject of major interest [7,9,11,14–17]. Lapis lazuli is a rock consisting of several micrometer-scale-size mineral phases, such as lazurite, diopside, wollastonite, sodalite, calcite, etc. [9], therefore micro-analysis techniques are very well suited for its detailed analysis. In this research work, the combination of IL microscopy, IL spectroscopy and micro-PIXE has been used to characterize the structure and mineral phases of a natural lapis lazuli sample from Afghanistan. Herein, the IL experiment was performed with a wide beam to identify the minerals of the sample, which were then studied by IL spectroscopy, using focused ion beam well within the mineral of interest, and micro-PIXE techniques.

2. Materials and methods

The lapis lazuli sample is supposed to come from Afghanistan and was provided from a gemstone center in Tehran. All the measurements were performed using the microbeam facility of

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* Corresponding author.
E-mail address: tnikbakht@aeoi.org.ir (T. Nikbakht).

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the Van de Graaff Laboratory of Tehran [18], which is based on an Oxford microbeam triplet setup. The micro-PIXE measurements were performed using a proton beam of 2 MeV energy and ~20 pA current, with a spot size of 10 × 10 μm^2 on the sample surface. An area of 1.2 × 1.2 mm^2 on the sample was scanned for ~30 min, while a smaller part of which (1 × 1 mm^2), in accordance with the IL analyzed area, was selected for further investigations. The characteristic X-rays were detected by a Si(Li) detector with 145 eV energy resolution at 5.9 keV. The data of the micro-PIXE experiment was analyzed by means of OM-DAQ 5.1 [19] and GUPIXWIN 2.2.0 [20], which provided the elemental maps and concentrations of the detected elements, respectively.

The reaction chamber was equipped with an optical microscope mounted at 45° to the beam direction. A slightly focused proton beam of 2 MeV energy with a 0.5 × 0.5 mm^2 profile on the sample surface and a current of about 1 nA was applied for acquisition of the IL images. The IL images of the sample were captured by means of an OPTIKA PRO 5 CCD, which was located at the focal point of one of the objective lenses of the microscope. By changing the beam position on the sample, the images of 12 adjacent pieces of the sample, corresponding to the analyzed area in micro-PIXE experiment, were captured separately. Considering the dimmer boarders of the IL images, the adjacent captured images partly overlapped each other. The IL images were then merged together to reveal the distribution of the different minerals of the sample. Finally an area of ~1 × 1 mm^2 on the sample surface, corresponding to the analyzed area by the micro-PIXE experiment, was selected for further analyzes.

A collimating lens of 25 mm focal length was connected to the microscope by means of an adapter to collect the luminescence of the sample and transmit it to a spectrometer through a fiber optic of 400 μm diameter. The spectrometer was an AvaSpec-ULS2048L with 25 μm slit size and 1.4 nm resolution in the wavelength range of 200–1100 nm, cooled down to 3 °C. Such optical setup provides the possibility of collecting both the IL spectroscopy and microscopy data of the sample. After capturing the IL images, IL spectra of different minerals in the sample were collected for an integration time of 30 s. Then, in order to collect the IL spectra of the single phases of the gemstone, the beam was focused to a spot size well within the desired area and spectra were collected for 20–50 s. All the measurements were carried out at room temperature. The Origin Pro 2015 b9.2.214 (OriginLab, Northampton, MA) software was used to analyze the luminescence spectra.

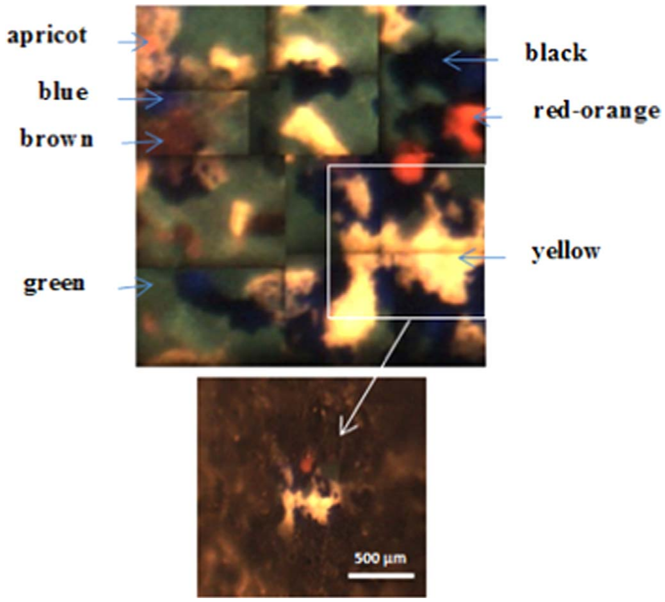

Fig. 1. The IL image of an area of ~1 × 1 mm^2 on the lapis lazuli sample surface, obtained using a slightly focused proton beam of 2 MeV energy. The pictures were captured by the CCD camera. The areas are labeled based on their dominant colors. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

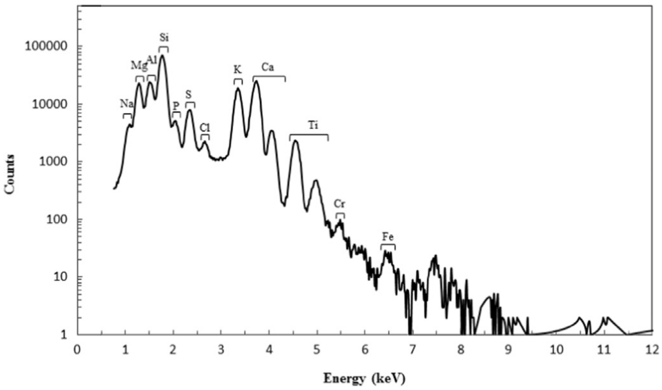

Fig. 2. The micro-PIXE spectrum for an area of almost 1 × 1 mm^2 on the surface of the lapis lazuli sample. The positions of the major elements are exhibited in the spectrum.

3. Results and discussion

The IL image of an area of almost 1 × 1 mm^2 on the sample under study is shown in Fig. 1. It can be viewed that the IL image reveals the texture of the sample with the colorful areas representing its different mineral phases. Seven areas of different dominant colors can be distinguished in the IL image, i.e. black (~15.9%), blue (~3.0%), green (~36.5%), red-orange (~2.1%), brown (~2.5%), yellow (~13.6%), and apricot (~2.3%). The sizes of different colorful areas, which are indicated in parentheses, are calculated by means of ImageJ [21]. The remaining area (~24.1%) consists of mixed colors and will not be discussed in the current work. Regarding lapis lazuli as a complex heterogeneous gemstone, the micro-PIXE experiment provides both the elemental maps and concentrations of the elements in different mineral phases of the sample. Such information allows reconstructing the distribution of the phases and provides the elemental information for analyzing the IL data. A typical X-ray spectrum of the lapis lazuli sample acquired for the area represented in Fig. 1 (1 × 1 mm^2) is shown in Fig. 2, with the positions of its major elements. Also, the elemental maps of most of the major elements, which were produced by means of OM-DAQ, are exhibited in Fig. 3, where they are compared with the IL image.

Experimental data need to be categorized based on the minerals of the sample, which typically correspond to different colorful areas of the IL image, as shown in Fig. 1 (in principle, we cannot exclude that different minerals can have similar IL bands). The relative elemental concentrations of different colorful areas of the IL image, which were calculated by means of GUPIXWIN, are presented in Table 1. Regarding the high statistics required for distinguishing the trace elements of the minerals, almost the data of the whole area attributed to each mineral must be analyzed to extract its elemental composition. The smaller the size of an area, the lower the statistics and hence the higher the limit of detection. However, the reported data in Table 1 are inevitably affected by some factors such as possible existence of more than one mineral in the beam path, selection of the areas attributed to different minerals in the elemental maps and substitution of trace elements for intrinsic cations of the minerals. Therefore, in order to minimize the uncertainties in the stoichiometries, small uniform areas of about 50 × 50 μm^2 were