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Ion beam analysis of rubies and their simulants

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ABSTRACT

Ion beam analysis (IBA) is a set of well known powerful analytical techniques which use energetic particle beam as a probe. Among them, two techniques are suitable for gemological analysis, i.e., Particle Induced X-rays Emission (PIXE) and Ionoluminescence (IL). We combine these two techniques for the investigations of rubies and their simulants. The main objective is to find a reference fingerprint of these gemstones. The data are collected from several natural rubies, synthetic rubies, red spinels, almandine garnets and rubellite which very much resemble and are difficult to distinguish with the gemologist loupe. From our measurements, due to their different crystal structures and compositions, can be clearly distinguished by the IL and PIXE techniques. The results show that the PIXE spectra consist of a few dominant lines of the host matrix elements of each gemstone and some weaker lines due to trace elements of transition metals. PIXE can easily differentiate rubies from other stones by evaluating their chemical compositions. It is noticed that synthetic rubies generally contain fewer impurities, lower iron and higher chromium than the natural ones. Moreover, the IL spectrum of ruby is unique and different from those of others stones. The typical spectrum of ruby is centered at 694 nm, with small sidebands that can be ascribed to a Cr^{3+} emission spectrum which is dominated by an R-line at the extreme red end of the visible part of the electromagnetic spectrum. Although the spectrum of synthetic ruby is centered at the same wavelength, the peak is stronger due to higher concentration of Cr and lower concentration of Fe than for natural rubies. For spinel, the IL spectrum shows strong deformation where the R-line is split due to the presence of MgO. For rubellite, the peak center is shifted to 692 nm which might be caused by the replacement of Mn^{3+} at the Al^{3+} site of the host structure. It is noticed that almandine garnet is not luminescent due to the idiochromatic nature of the stone.

1. Introduction

A natural gemstone, a crystalline form of mineral, is desired for its beauty, valuable in its rarity and durable enough to be enjoyed for generations. Gemologists may face two problems in the identification of gemstone. The first is the determination of whether it is natural or synthetic and real or substitute. Synthetic ones are much less valuable, but may not distinguished by conventional tests. Also there are several natural gemstones very much resemble to ruby and are difficult to identify with the gemologist loupe. The second problem is the determination of the source of gems that can have a profound impact on their market value. Therefore, it is important to strengthen the conclusions of the gemologist observations with the chemical composition of the gemstones. Among a wide variety of analytical methods applied to gemstones, such as Raman microspectroscopy, neutron activation analysis, and energy dispersive X-ray fluorescence spectrometry, ion beam analysis (IBA) techniques have several extra advantages in addition to the generally known non-destructiveness and good spatial resolution.

Ion beam analysis (IBA) technique has just been introduced for the non-destructive elemental analysis in Thailand [1]. They constitute a set of powerful analytical techniques of which at least two techniques are suitable for gemologists; i.e. Particle Induced X-rays Emission (PIXE) and Ionoluminescence (IL). These techniques are potential sensitive tools for both qualitative and quantitative analysis of minerals [2]. The emitted X-rays, in the case of PIXE, originate from the de-excitations between inner atomic

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levels, induced by the MeV proton beam and therefore, are only related to the nature of the chemical element. On the other hand, in the case of IL, the near IR to UV radiations corresponds to outer energy levels of atoms or molecules that are affected by the chemical environment of the atoms. Accordingly, the IL spectrum also depends on the host of the trace elements. Therefore, the results from these measurements can provide a useful fingerprint pattern for a large number of gemstones.

Ruby is generally known as the most valuable of all color gemstones. It is the mineral corundum (Al_2O_3) that has apparent color from a pink to blood-red. Corundum is allochromatic, which means that the chemistry of their basic formula does not cause any selective absorption so that they are clear or colorless in the pure state. In these types of gems, it is the traces of impurities that act as chromophores. As for rubies, the red color is caused mainly by the presence of a few percent of the element chromium (Cr). Prices of rubies are primarily determined by their color. The brightest and most valuable red color called "pigeon's blood" color prevails over other rubies of similar quality. However, some stones appear very similar to rubies and are hard to distinguish with the gemologist loupe. Such stones are, for examples, red spinel, almandine garnet and rubellite. Therefore, PIXE and IL were applied for investigations of various red gemstones in the present study with the main objective to distinguish the natural rubies from their imitations and substitutes.

2. Experimental details

Both cut and uncut of ~100 rubies from various deposits, 30 red spinels, 1 rubellite and 10 almandine garnets were investigated. PIXE and IL electromagnetic radiation were induced by a proton beam accelerated to 2 MeV by a 1.7-MV tandem accelerator of Chiang Mai University. The proton ions were generated from titanium hydride (TiH_2) powder in a negative ion Cs-sputter source. The beam was collimated with a diameter of ~1 mm, and the beam current on the sample was less than 10 nA. Base pressure in the vacuum chamber was about 6×10^{-6} mbar. Each gem was mounted on the head of a small bolt with super epoxy adhesive and was screwed into a sample holder which can hold as many as 50 gems. By this way the top surface of each stone can easily be adjusted to the same level. For PIXE, X-rays were detected by a Si(Li) detector located at 120° to the beam direction. Multichannel analyzer card, connected to a computer, was used for data accumulation. In the experiment, a 74-μm mylar foil thickness, with a hole of 0.38% of the active area of the detector, was placed in front of the beryllium window of the detector as an absorber in order to reduce the count rate caused by elements of low atomic numbers. A flood of electrons from an electron gun was used in order to reduce the bremsstrahlung continuum background from due to the charging of insulator sample like these gemstones. Each measurement took around 10 min and the spectra were analysed by the GUPIXWIN software [3]. For IL, the emitted light was recorded by the Fiber Optics spectrometer (Model S2000, Ocean Optics, Inc.) placed outside the analysis chamber. The configuration featured a 600 lines/mm grating (set for 300–950 nm), 2014-element linear silicon CCD array detector, and a 1000 μm diameter optical fiber for signal collection. Optical resolution of the system is ~1.3 nm FWHM. The spectra were displayed by OOIBase32–32 bit Spectrometer operating software [4]. In order to collect a satisfying emission peak, each spectrum was recorded at about five seconds.

3. Results and discussions

Fig. 1 displays a collection of five PIXE spectra from natural and synthetic rubies and various others red gemstones. The results show that the spectra consist of a dominant line of the host matrix elements of each gemstone and a few weak lines due to the trace elements of transition metals. PIXE can easily differentiate rubies from other stones on the basic of their chemical compositions. The oxide compositions of rubies from various origins and of rubies imitations and substitutes are summarized in Tables 1 and 2, respectively. Fig. 2 displays the IL spectra of these gemstones, in the wavelength region between 600 and 800 nm. It is clear that IL spectrum of rubies are different from others stones.

3.1. Rubies and synthetic rubies

Ruby crystal is in hexagonal and rhombohedral system and has hardness of 9.0 on the Mohs Hardness Scale. The chemical formula of rubies is Al_2O_3 with Al ~ 53 wt.% and O ~ 47 wt.% [5]. From our PIXE measurement, the strong X-ray peak of Al is clearly seen and the peaks of Cr and Fe and other trace elements, e.g. Ti, V, and Ga are also observed. We have analysed natural rubies from four origins and found that they exhibit similar levels of Ti, V, and Ga but a markedly different Cr and Fe concentrations (Table 1). The wide variations in Cr and Fe contents are reflected in the range of color, from paler to stronger in red. It is useful to relate between two concentrations of any couple of key trace elements in a *x–y* plot to see if any population field appears. Examples of such plots are shown

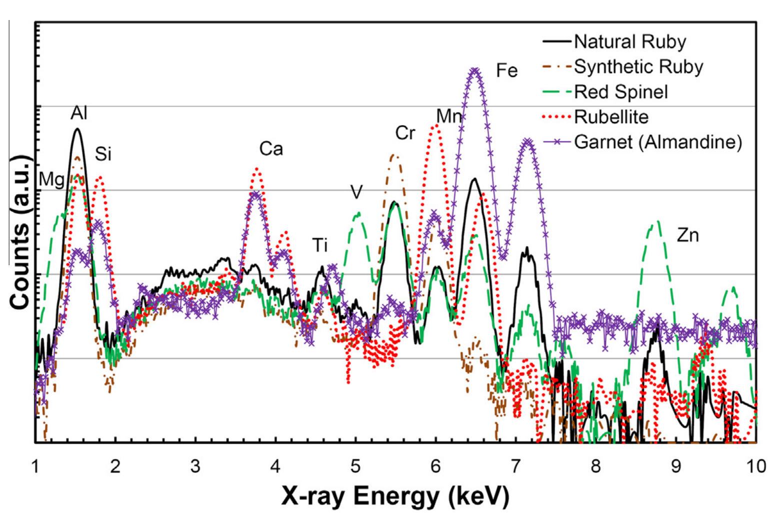

Fig. 1. PIXE spectra of a natural ruby with synthetic ruby and resembling gemstones.