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Fe²⁺ and Fe³⁺ oxidation states on natural sapphires probed by X-ray absorption spectroscopy

Natthapong Monarumit^a, Wiwat Wongkokua^b, Somruedee Satitkune^{a,*}

^aDepartment of Earth Sciences, Faculty of Science, Kasetsart University, Bangkok, 10900, Thailand

^bDepartment of Physics, Faculty of Science, Kasetsart University, Bangkok, 10900, Thailand

Abstract

Sapphire is the inorganic gemstone in varieties of gem corundum with the pure alpha-alumina (α -Al₂O₃) structure showing colorless. The various colors of sapphire are caused by some trace elements such as Cr, Fe, and Ti. Natural sapphires occur in different geological origins such as basaltic and metamorphic host rocks. High-quality sapphires contain low inclusion. The sapphire qualities are based on their sources that are hardly identified by the gemological instrument. In this study, X-ray absorption spectroscopy (XAS) focused on X-ray absorption near edge structure (XANES) technique using the Synchrotron radiation is employed for identifying the origins of sapphire samples. In particular, Fe *K*-edge XANES spectra are applied to analyze the Fe oxidation states on sapphires. As the results, we conclude that there were the Fe²⁺ from some mineral inclusions and Fe³⁺ which substitute Al³⁺ on the sapphire structure from both basaltic and metamorphic sources.

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1. Introduction

Natural alpha-alumina (α -Al₂O₃) known as corundum applied for gem materials such as ruby and sapphires¹. Pure corundum is colorless, however, the other color of corundum caused by the vacancies of trace elements as the

* Corresponding author. Tel.: +66-2940-6966; fax: +66-2940-6966.

E-mail address: fscisrd@ku.ac.th

structural defect^{2,3}. For example; Cr³⁺, Fe-Ti pairs, and Fe³⁺ produced red, blue and yellow, respectively. Corundum crystals with colors except red are called sapphires. Sapphires have been originated in various geological origins that are related to either basaltic or metamorphic sources⁴. Nowadays, the identification of sapphire sources is based on the experiences of gemologists. The color hue of sapphires is one of the factors to classify their sources and their qualities¹. The defect properties such as dielectric constant were applied to study the causes of color in sapphires⁵. Initially, the Fe atoms in sapphire structure play an important role to produce the different coloration². However, there were two Fe oxidation states such as Fe²⁺ and Fe³⁺ proposed to create the color of sapphires probed by UV-Vis spectroscopy and electron spin resonance (ESR)^{2,3,6}. Therefore, the Fe oxidation states on natural sapphire structures could be analyzed for better understanding the coloration of sapphire.

In this study, the Fe oxidation states on natural sapphires collected from different origins will be measured by X-ray absorption spectroscopy (XAS) using the Synchrotron radiation.

2. Materials and Methods

2.1. Sample preparation

The natural sapphire samples were collected from various geological origins, i.e., basaltic and metamorphic ones as shown in Figure 1. For basaltic sapphires, the samples were selected from Thailand whereas the metamorphic ones were selected from Sri Lanka gem fields. The samples were polished in gem-trade level and found the c axis by polariscope to precisely record the direction of X-ray beam for XAS measurement, such as parallel and perpendicular to the c axis. Moreover, there were the Fe-oxide standards in powder form for referring the oxidation states including Fe foil (as Fe⁰), FeO (as Fe²⁺), Fe₂O₃ (as Fe³⁺) and Fe₃O₄ (as Fe^{2+,3+}).



Fig. 1. The natural sapphire samples in this study

2.2. X-ray absorption spectroscopy

XAS measurement of the natural sapphire samples focused on Fe *K*-edge using XANES technique in fluorescence mode. The Fe *K*-edge XANES spectra were measured at XAS Beamline-8 station, located in the Synchrotron Light Research Institute (SLRI), Thailand, employing the synchrotron radiation beam from eight bending magnets⁷. The XAS technique is suitable for gemstone because of the non-destructive method⁸. In this study, the XANES measurement was set to detect the spectra at Fe *K*-edge, which calibrated at 7112 eV referred to the binding energy (E_0) of Fe⁰ oxidation states. The Ge (220) double crystal monochromator was used with 0.1 meV to 0.3 meV energy resolution depended on the width of entrance slit. The specific parameters of this measurement for the sapphire samples were -20 eV to +120 eV with 0.2 eV energy step width and 5 s derivative time using the 13-channel array germanium detector to obtain the spectra for four times scan.

Principally, the absorption coefficient of the sapphire samples measured in fluorescence mode could be calculated by the Eq. 1⁹.

$$I_f / I_0 = \mu x \quad (1)$$

Besides, the Fe *K*-edge XANES spectra of Fe-oxide standards were carried out using the transmission mode. The absorption coefficient was calculated by the Eq. 2⁹.

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