Abstract

Yellow color in gem corundum is commonly caused by Fe$^{3+}$ impurity replacing Al$^{3+}$ in the Al$_2$O$_3$ structure. For two decades beryllium-assisted heat treatment has been introduced to produce yellow sapphires from colorless, green, or light blue sapphires. The roles of beryllium atoms in corundum structure have been proposed in different ways either triggering structural defects or being as catalysts. Thus, the research experiments were conducted to evaluate these contradictions by applying the UV–vis excitation spectra and Fe K-edge x-ray absorption near edge structure spectra (XANES) of the samples, in combinations with Tauc plots of the UV–vis absorption spectra. The trace element content of the samples was analyzed by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). As a result, iron impurity in the samples has been confirmed as Fe$^{3+}$ by XANES spectra, and hence, revealed as the cause of yellow color in natural yellow sapphire samples. Besides, the absorptions at 423 nm, 457 nm, 487 nm and 553 nm and emissions at 609 nm and 841 nm of Fe$^{3+}$–Be$^{2+}$ mixed donor states were detected by UV–vis excitation, which is the novel finding on the origin of yellow coloration in beryllium-treated sapphires. Therefore, an energy band model for mixed Fe$^{3+}$–Be$^{2+}$ donor states is proposed to be responsible for the yellow color center in beryllium-treated yellow sapphires, comparable to Fe$^{3+}$ and Fe$^{3+}$/Fe$^{3+}$ states for the natural yellow sapphires commonly contain high iron.

Introduction

Corundum is α-Al$_2$O$_3$ in which its color varieties can be used as precious gemstones. The naturally colorless ones normally contain rare impurities, whereas those with various colors are subjected to some trace elements such as Fe, Ti and Cr in the corundum structure. A considerable amount of iron impurity is responsible for yellow coloration in sapphire [1]. The cause of yellow color in sapphire normally occurs when Fe$^{3+}$ substitutes Al$^{3+}$ in the corundum structure [2, 3]. This process can be described in terms of a structural defect, which affects the energy band gap of the corundum resulting in modification of its physical appearance such as color [4]. Moreover, yellow-colored sapphires can also be produced from colorless, green or light blue varieties by heating with beryllium. Thus, beryllium atoms were suggested to have caused structural defects in the corundum structure when undergone heating with beryllium compound in the oxidizing atmosphere [5, 6].

Generally, the causes of color in corundum have been studied by spectroscopic techniques such as UV–vis-NIR spectroscopy, electron spin resonance (ESR) and Mössbauer spectroscopy [7–13]. The trace element concentrations could be analyzed by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) or the energy dispersive x-ray fluorescence (EDXRF) [14, 15]. In the beryllium-treated sapphire case, the content of beryllium can be measured by LA-ICP-MS. Beryllium has been proposed to cause either yellow color center in beryllium-treated yellow sapphire [5, 6] or as being a catalyst for the transformation of Fe$^{2+}$ to Fe$^{3+}$ [11]. Therefore, the role of beryllium to cause yellow coloration has not yet been conclusively understood.
X-ray absorption spectroscopy (XAS) is a powerful technique to study the local atomic environment of an investigated atom. Besides, XAS is a non-destructive method and suitable for gemological research [16–19]. The XAS spectrum can be divided into two parts including the x-ray absorption near edge structure (XANES) and extended the x-ray absorption fine structure (EXAFS) [20]. However, the XAS technique is not suitable for detecting light elements such as Be.

In this work, the XANES spectra of Fe K-edge were studied to reveal the Fe oxidation states in natural yellow sapphire samples and beryllium-treated ones. The amounts of trace elements in the samples before and after beryllium heat treatment were measured by LA-ICP-MS. The results are evaluated and discussed by calculating the energy gaps of the samples using Tauc plots from the UV–vis absorption spectra in combination with the UV–vis excitation spectra to characterize the role of beryllium in beryllium-treated yellow sapphire.

Materials

Figure 1 represents sapphire samples of two rough natural yellow sapphires (NYS), and three rough light blue sapphires (BES) which later have been heat-treated with ground BeO mixing in an alumina crucible introduced into an electric furnace then heating up to 1715 °C under an oxidizing atmosphere for 80 h. The BES samples are therefore becoming yellow sapphires after the treatment. For NYS, both samples were collected from Nam Yuen Sub-District, Thailand (NYS 1 and NYS 2) while the BES samples (originally light blue) were from Thailand (BES 1) and Sri Lanka (BES 2 and BES 3). Geologically, the sapphire samples from Thailand are basaltic related, i.e. having higher iron content compared to those of metamorphic sapphire samples from Sri Lanka. The samples were polished for surface adjustment before the experimental procedure.

Methodology

The quantitative chemical elements of the samples were analyzed by LA-ICP-MS at the Gem and Jewelry Institute of Thailand (Public Organization) to detect some trace elements (Be, Fe, Ti and Cr) involving in the causes of sapphire coloration.

UV–vis absorption spectra of the sapphire samples were measured perpendicular to the c axis in transmission mode using the PerkinElmer UV–vis spectrometer (Lambda™ 650 model) with an integrating sphere and the UV–vis excitation spectra of the samples were obtained by Avantes spectrometer.

XAS experiments focused on Fe K-edge XANES spectra were carried out at the Synchrotron Light Research Institute (Beamline-8; XAS station), Nakhon Ratchasima Province, Thailand [20] for analyzing the Fe oxidation states in the samples.

In this study, the principal parameters set to perform Fe K-edge XANES measurement include Ge(220) double crystal monochromator, a 13-channel array germanium detector as well as the vacuum condition in ion chambers. The Fe standard materials in powder form were used for a reference spectra composing of Fe foil, FeO and Fe$_2$O$_3$ referred to Fe$^0$, Fe$^{2+}$ and Fe$^{3+}$ oxidation states, respectively. Initially, the Fe foil standard were used to calibrate the photon energy of Fe K-edge at 7112 eV followed by other standard materials measured in transmission mode. Next step, the natural yellow sapphires and beryllium-treated yellow sapphires were measured for Fe K-edge of the XANES spectra in fluorescent mode by the specific parameters including the photon energy scan of 7092 eV to 7232 eV; the photon energy steps were 2 eV and 0.2 eV; the time steps were 3 s. Finally, the XANES data processing was performed by Athena program [21, 22].
Results and discussion

The content of trace elements was analyzed by LA-ICP-MS as shown in Table 1. Relative standard uncertainties are 20%, 52%, 7% and 25% for Be, Fe, Ti and Cr, respectively. The results indicated that the (untreated) natural yellow sapphires (NYS 1, NYS 2) revealed high Fe content (>10,000 mg kg\(^{-1}\)) and low Be, Ti and Cr content. The light blue samples contain moderate (\(~3000\) mg kg\(^{-1}\)) to low (\(~550\) mg kg\(^{-1}\)) iron concentrations of those of NYS ones. For the Be-heat treated sapphires (BES 1, BES 2, BES 3), Be atoms diffused into the sapphire structure, and the samples turned from light blue to yellow [6]. Sapphire samples containing both moderate and

| Samples | Photo | Be (mg kg\(^{-1}\)) | Fe (mg kg\(^{-1}\)) | Ti (mg kg\(^{-1}\)) | Cr (mg kg\(^{-1}\)) |
|---------|-------|---------------------|---------------------|---------------------|---------------------|
| NYS 1   |       | 2.1                 | 12478.5             | 15.2                | 6.3                 |
| NYS 2   |       | 2.2                 | 16797.9             | 45.2                | 6.9                 |
| BES 1 (before treatment) |       | 0.4                 | 3313.0              | 35.3                | 4.3                 |
| BES 1 (after Be-treatment) |       | 13.5                | 3765.0              | 56.8                | 3.4                 |
| BES 2 (before treatment) |       | 0.9                 | 536.0               | 136.9               | 12.7                |
| BES 2 (after Be-treatment) |       | 7.9                 | 595.2               | 173.5               | 28.3                |
| BES 3 (before treatment) |       | 0.6                 | 561.8               | 214.7               | 3.7                 |
| BES 3 (after Be-treatment) |       | 7.3                 | 534.3               | 51.2                | 3.9                 |

Table 1. Trace element (Be, Fe, Ti, Cr) content in representative sapphire samples measured by LA-ICP-MS.
low Fe concentrations show yellow color after Be treatment. The role of Be as a catalyst could be ruled out because the concentration of Be was found to significantly increase after Be treatment in all samples.

The normalized Fe K-edge XANES spectra of Fe standard materials and yellow sapphire samples were shown in figure 2 (a). The standards Fe foil, FeO and Fe₂O₃, indicating Fe⁰, Fe²⁺ and Fe³⁺ oxidation states, were designated at 7112 eV, 7119 eV and 7124 eV, respectively. Moreover, the presence of pre-edge features had been also used to differentiate the Fe oxidation states. The absorption edge positions of all samples were indicated at 7124 eV relating to the Fe³⁺ oxidation state regardless of different Fe concentration. The pre-edge peak positions at 7115 eV were displayed in all spectra and similar to those of Fe₂O₃ confirming to be Fe³⁺ in their α-Al₂O₃ structures [23]. Although the Fe K-edge of samples has not been measured before treatment, the oxidation state other than Fe³⁺ of untreated sapphire samples has never been observed from any of previous research experiments [24–26]. Besides, the first derivative of the XANES spectra was plotted to confirm the absorption edge positions of Fe standard materials and yellow sapphire samples and shown in figure 2 (b). The different Fe XANES spectra could be due to the Fe concentration that could affect the different edge jumps. However, Be heat treatment can cause the development of yellow coloration in both kinds of samples.

The features of pre-edge for BES 1 and BES 3 were similar to the shoulder of the metallic spectrum. For quantitative analysis, we carried out the linear combination fit (LCF) of all spectra with references: Fe foil, Fe²⁺ and Fe³⁺ as shown in table 2. It is better to use appropriate references for Fe²⁺ and Fe³⁺ with local coordination similar to what is expected in sapphire. However, using FeO and Fe₂O₃ is a moderate approximation. Such LCF was performed in Athena software by derivative within an energy range of −20 eV below to +30 eV above the edge. The fitting results show that the spectra were a combination of Fe foil and Fe³⁺ without Fe²⁺. The presence

![Figure 2. Fe K-edge XANES spectra of Fe-standard materials, natural yellow sapphire and beryllium-treated yellow sapphire samples (a) and associated first derivative spectra (b).](image)

| Sample | Fe foil; Fe⁰ | FeO; Fe²⁺ | Fe₂O₃; Fe³⁺ |
|--------|-------------|-----------|-----------|
| NYS 1  | 0.138 ± 0.035 | 0.000 ± 0.038 | 0.862 ± 0.052 |
| NYS 2  | 0.067 ± 0.029 | 0.000 ± 0.031 | 0.933 ± 0.043 |
| BES 1  | 0.395 ± 0.025 | 0.000 ± 0.027 | 0.605 ± 0.037 |
| BES 2  | 0.071 ± 0.031 | 0.000 ± 0.034 | 0.929 ± 0.046 |
| BES 3  | 0.513 ± 0.022 | 0.000 ± 0.023 | 0.487 ± 0.032 |
of Fe foil in the results could be caused by the overlap of the metallic Fe K-edge at 7112 eV and the pre-edge of Fe$^{3+}$ at 7115 eV. The high weights of Fe foil to Fe$^{3+}$ for BES 1 and BES 3 were influenced by the relatively broad bands of the pre-edge and low edge jump of the spectra due to low Fe concentrations of the samples.

UV–vis spectra of the samples with Tauc Plots shown in figure 3 indicate that the absorption peaks causing yellow coloration in natural yellow sapphires (NYS) were different from those in beryllium-treated ones (BES).
The single Fe$^{3+}$ at 388 nm, as well as the Fe$^{3+}$/Fe$^{2+}$ pairs at 377 nm and 450 nm, were shown with the energy bandgap ($E_g$) about 3.45 eV. For beryllium-treated yellow sapphires; the Fe$^{3+}$/Ti$^{4+}$ pairs absorptions at 580 nm and 710 nm relating to blue color were slightly decreased due to Fe$^{3+}$/Ti$^{4+}$ mixed acceptor states [24] became neutral by the Be donor atoms. The chemical coordination state of Ti in untreated sapphire was Ti$^{4+}$ and unchanged under Be treatment [24]. Thus, likely liberated Fe$^{3+}$ forms the mixed Fe$^{3+}$-Be$^{2+}$ donor states. The energy band gaps of the BES samples remain significantly unchanged before and after Be-heated treatment ($E_g = 3.98$ eV and 3.99 eV, respectively).

The causes of yellow and brown coloration in Be-treated sapphires have been investigated on natural and synthetic colorless sapphires [6, 27]. The yellow coloration was activated in natural colorless sapphires with a relatively low Fe concentration (∼350 mg kg$^{-1}$) while the brown color was activated in the synthetic colorless sapphire without iron. Hence, the yellow coloration could reasonably be caused by the formation of Fe$^{3+}$-Be$^{2+}$ pairs.

The UV–vis excitation spectrum of beryllium-treated yellow sapphires was shown in figure 4. The presence of excitation peaks at 423 nm, 457 nm, 487 nm, 553 nm, 609 nm and 841 nm on Be-heated samples was distinct from the absorption peaks. To confirm the observation of these peaks, the spectra were multi-peak fitted. Therefore, it could be suggested that the peak positions at 423 nm, 457 nm, 487 nm and 553 nm are related to Fe$^{3+}$, and Be$^{2+}$ shown with the emissions at 609 nm and 841 nm in beryllium-treated yellow sapphires. Previously, a Be$^{2+}$ donor state was found in beryllium-treated synthetic ruby via UV–vis excitation spectra at 475 nm [28]. However, the peak positions could be shifted by the interaction between Fe$^{3+}$ and Be$^{2+}$ becoming Fe$^{3+}$-Be$^{2+}$ mixed donor states that responsible for the yellow color center in yellow sapphire.

According to the results, the causes of yellow color in beryllium-treated sapphires could be described by the color center in energy band theory. For natural yellow sapphires with considerably high iron content, the yellow color is caused by the Fe$^{3+}$ and Fe$^{3+}$-Fe$^{3+}$ states at 3.20 eV and both of 2.76 eV, 3.29 eV corresponding to absorptions at 388 nm and both of 450 nm, 377 nm, respectively. These states were stable, located in the energy band gap of 3.45 eV as shown in figure 5(a). For sapphire samples with lower iron content, the yellow color in beryllium-treated sapphires is caused by the color center produced by Fe$^{3+}$-Be$^{2+}$ mixed donor states. Four Fe$^{3+}$-Be$^{2+}$ mixed donor states located at 2.93 eV, 2.71 eV, 2.55 eV and 2.24 eV corresponding to 423 nm, 457 nm, 487 nm and 553 nm in UV–vis excitation spectrum, respectively; which were shown as broadening of the excitation peaks due to long lifetime of the donor states and influence for producing yellow by the absorption of purple, blue and green region within its energy band gap of 3.99 eV. Thus, yellow coloration in sapphires resulted from beryllium treatment was effectively caused by the electron transition from Fe$^{3+}$-Be$^{2+}$ mixed donor states located inside the energy bandgap; to the conduction band shown in figure 5(b). Moreover, the energy was released as Fe$^{3+}$-Be$^{2+}$ emission inside the energy bandgap ($E_g = 3.99$ eV) at 1.47 eV (841 nm) and 2.04 eV (609 nm) with remarkable energy states inside the conduction band at 4.02 eV and 4.28 eV respectively.
Conclusion

The energy band model to describe the causes of yellow color center in beryllium-treated sapphires that are related to beryllium diffusion in the sapphire structure as a result of Fe$^{3+}$-Be$^{2+}$ mixed donor states has been proposed. These states are inside the energy band gap located at 2.93 eV, 2.71 eV, 2.55 eV and 2.24 eV corresponding to 423 nm, 457 nm, 487 nm and 553 nm bands of UV–vis excitation spectra, respectively. This process is responsible for producing the yellow color in beryllium-treated sapphires. Besides, the yellow color in those natural yellow sapphires containing high iron is confirmed to be caused by Fe$^{3+}$ and Fe$^{3+}$-Fe$^{3+}$ pairs and these states are stable in the energy bandgap.

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References

[1] Häger T 2001 Proc. Int. Workshop Material Characterization by Solid State Spectroscopy: The Minerals of Vietnam 24–37
[2] Nassau K 2001 The Physics and Chemistry of Color 2nd edn (New York: Wiley)
[3] Fritsch E and Rossman G R 1988 Gems. Gemol. 24 3–15
[4] Fritsch E and Rossman G R 1988 Gems. Gemol., 24 81–102
[5] Emmett J L et al 2003 Gems. Gemol. 39 64–135
[6] Pisutha-Arnond V, Häger T, Wathanakul P and Atichat W 2004 J. Gemm. 29 77–103
[7] Lehmann G and Harder H 1970 Am. Min. 55 98–105
[8] Faye G H 1971 Am. Min. 56 344–8
[9] Schmetzer K, Bosshart G and Hanni H A 1983 J. Gemm. 18 607–22
[10] Udomkan N, Limsuwan P, Winotai P and Meejoo S 2005 Int. J. Mod. Phys. B 19 3273–84
[11] Limsuwan P, Meejoo S, Somdee A, Thamaphat K, Kittiauchawal T, Siripinyanond A and Krzystock J 2008 Chin. Phys. Lett. 25 1976–9

Figure 5. An energy band model of Fe$^{3+}$-Fe$^{3+}$ and Fe$^{3+}$ states in natural yellow sapphire with high iron (a) compared to Fe$^{3+}$-Be$^{2+}$ mixed donor states in beryllium-treated yellow sapphire (b).
[12] Mungchamnankit A, Kittiauchawal T, Kaewkhao J and Limsuwan P 2012 Procedia Engineering 32 950–5
[13] Molnár G, Homonnay Z, Vértes A, Borossay J, Serrano B and Iacconi P 2001 J. Phys. Chem. Solids 62 619–25
[14] Abduriyim A and Kitawaki H 2006 Gems Gemol. 42 98–118
[15] Bonizzoni L, Galli A, Spinolo G and Palanza V 2009 Anal. Bionanal. Chem. 395 2021–7
[16] Wongkokua W, Pongkrapan S, Dararatuna P, Thienprasert JT and Wathanakul P 2009 J. Phys.: Conf. Ser. 185 012054
[17] Jheeta K S and Jain D C 2007 African Physical Review 1 56–66
[18] Wilke M, Farges F, Petit P E, Brown E G Jr and Martin F 2001 Am. Min. 86 714–30
[19] Monarumit N, Notrawee N, Phlayrahan A, Promdee K, Won-In K and Satitkune S 2015 J. Appl. Spectr. 82 677–80
[20] Klysubun W, Sombunchoo P, Deenan W and Kongmark C 2012 J. Synchrotron Radiat. 19 930–6
[21] Newville M 2001 J. Synchrotron Radiat. 8 322–4
[22] Ravel B and Newville M 2005 J. Synchrotron Radiat. 12 537–41
[23] Gaudry E, Cabaret D, Saintavit C, Brouder C, Mauri F, Goulon J and Rogalev A 2005 J. Phys. Condens. Matter 17 5467–80
[24] Wongrawang P, Monarumit N, Thammaraj N, Wathanakul P and Wongkokua W 2016 Mat. Res. Exp. 3 026201
[25] Jivanantaka P, Monarumit N and Satitkune S 2018 J. Phys. Conf. Ser. 1144 012016
[26] Phlayrahan A, Monarumit N, Lhuaamporn T, Satitkune S and Wathanakul P 2019 J. Appl. Spectr. 86 810–6
[27] Pisutha-Arnond V, Hager T, Atichat W and Wathanakul P 2006 J. Gemm. 30 131–43
[28] Monarumit N, Lhuaamporn T, Satitkune S and Wongkokua W 2019 J. Appl. Spectr. 86 486–92