Applied Surface Science 403 (2017) 267–273

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Effect of fusion mixture treatment on the surface of low grade natural ruby

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A R T I C L E I N F O

Article history:
Received 9 August 2016
Received in revised form 21 November 2016
Accepted 17 January 2017
Available online 20 January 2017

Keywords:
Ruby
Fusion mixture
Photoluminescence spectra
Chromium concentration

A B S T R A C T

Improvement in aesthetic look of low grade natural ruby (gemstone) surface was clearly evident after fusion mixture treatment. Surface impurities of the gemstone were significantly reduced to give it a face lift. The processing consists of heat treatment (1000 °C) of the raw gemstone with fusion mixture (sodium and potassium carbonates), followed by hydrochloric acid digestion (90 °C) and ultrasonic cleaning.Both the untreated and the treated gemstone were characterized by X-ray diffraction, UV–vis spectroscopy (diffuse reflectance),photoluminescence and X-ray photoelectron spectroscopy. The paper consolidates the results of these studies and presents the effect of the typical chemical treatment (stated above) on the low grade natural ruby. While X-ray diffraction study identifies the occurrence of alumina phase in both the treated and the untreated gemstones, the UV–vis spectra exhibit strong characteristic absorption of Cr^{3+}at 400 and 550 nm wavelength for the treated gemstone in contrast to weak absorption observed for the untreated gemstone at such wavelengths, thus showing the beneficial effect of fusion mixture treatment. Peaks observed for the gemstone (for both treated and untreated samples) in the excitation spectra of photoluminescence show a good correlation with observed UV–vis (diffuse reflectance) spectra. Photoluminescence emission spectra of the untreated gemstone show characteristic emission at 695 nm for Cr^{3+} ion (as in alumina matrix), but its emission intensity significantly reduces after fusion mixture treatment. It is found that the surface of the fusion mixture treated ruby gemstone looks much brighter than the corresponding untreated surface.

1. Introduction

Gemstones have remained quite attractive sources for humankind over several thousands of years and got into use in jewellery and decorative items. Garnet, beryl, topaz, blue sapphire, diamond (C), ruby (Al_2O_3:Cr), and emerald ($Be_3Al_2Si_6O_{18}$:Cr) are some of the well-known gemstones used in jewellery.Both artificial as well as natural gems have similar chemical composition and crystal structure, but the market demand always lies more for natural ones, possibly due to astrological beliefs. In this study, natural ruby, available in the form of low grade gemstone, was chosen to improve aesthetic quality and make value addition. Ruby is a red variety gemstone from the multi-coloured corundum family. It contains α-alumina (Al_2O_3) phase in which small quantity of $Al^{3+}$is replaced by Cr^{3+} ions. Each Cr^{3+} ion is octahedrally surrounded by six O^{2-} ions. The surrounding octahedral environment affects the Cr^{3+} ion in such a way that it absorbs in yellow-green region to give red colour emission [1]. Very fine traces of other impurities like silica, carbon and iron are also found in natural ruby along with presence of inclusion like rutile [2]. Ruby possesses high heat-resistance, high melting point, high mechanical strength, high hardness and excellent chemical stability at ambient condition. Availability of good quality ruby in nature is scarce compared to other gemstones and many of them (rubies) are found in mines which are of low qualities. Therefore, it is felt necessary to improve the quality of low grade ruby gemstones collected from natural sources to meet the societal demand. There are many methods to improve the quality of natural ruby. Some of these include laser treatment, dyeing, surface coating, ion implantation [3], γ-irradiation, heat treatment, etc. Heating the stone at high temperature is one of most common conventional methods to improve the colour of natural ruby [4]. Now-a-days gemstones are treated with different kinds of chemical environment at high temperature for fracture filling [5,6] and removal of impurity patches [7]. Recently new effort has been made to improve the colour of ruby by treating it in the microwave oven [8]. In this paper authors have made effort to improve the colour of low grade natural ruby gemstone by heating it with fusion mixture to remove

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http://dx.doi.org/10.1016/j.apsusc.2017.01.167
0169-4332/

the surface impurities. Both untreated and fusion mixture treated ruby samples were characterized by several techniques and the results thus obtained are compared to assess the improvement occurring in the quality of gemstone.

2. Materials and methods

2.1. Heat treatment of natural low grade ruby gemstone with fusion mixture

Low grade natural ruby gem stones in the size range of 5–10 mm were collected from Dumerpadar village of Kalahandi district, Odisha, India. These were designated as untreated gemstones. Untreated gemstone was taken in a platinum crucible and heated at 1000 °C for 4 h and this was denoted as heat treated gemstone. For fusion mixture treatment, the untreated gemstone was taken in a platinum crucible and was mixed with fusion mixture (1:1 molar ratio of anhydrous sodium and potassium carbonates, Qualigen LR grade). The mixed sample was then heated in a muffle furnace (Relek Pvt. Ltd., Model TQ1164). Temperature of the sample was gradually raised to1000 °C where it was held for 2 h after stabilization. At this temperature, the complex silicates were broken in to form of sodium/potassium aluminium silicate [9] which caused leaching of the gemstone (ruby) surface.The resulting sample was then allowed to cool and subjected to hydrochloric acid digestion at 90 °C followed by ultrasonic cleaning to remove surface sticky impurities (complex silicates) formed during the course of fusion mixture treatment. The sample thus obtained by this method is denoted as fusion mixture treated sample.

The chemical reaction occurred during the fusion mixture treatment of ruby surface is viewed as follows. Sodium and potassium carbonates react with silica material to form their corresponding di-silicates and metal silicates with evolution of carbon dioxide.

$$Na_2CO_3 + nSiO_2 \rightarrow (Na_2O) \bullet (SiO_2)_n + CO_2(g).K_2CO_3CO_2(g) \cdot K_2CO_3 + n\,SiO_2 \rightarrow (K_2O) \bullet (SiO_2)_n + CO_2(g)$$

Aluminum oxide reacts with sodium carbonate to produce sodium aluminate and carbon dioxide.

$$Al_2O_3 + Na_2CO_3 \rightarrow 2NaAlO_2 + CO_2$$

Chromium (III) oxide present in the corundum matrix also reacts with sodium carbonate in the presence of air to produce sodium chromate and carbon dioxide.

$$2Cr_2O_3 + 3O_2 + 4Na_2CO_3 \rightarrow 4Na_2CrO_4 + 4CO_2$$

Sodium carbonate and potassium carbonate behave with silica in different manners. Sodium ion spreads over silica strain while potassium ion tends to drill into the grain. Potassium carbonate reacts more rapidly with silica material compared to sodium carbonate. But the mixture of these two reactants attacks the ruby surface more rapidly than either of them [9]. Hence, fusion mixture was chosen here to remove impurities in order to increase the effectiveness of colour improvement in low grade natural ruby surface. Sillimanite is a complex aluminium silicate matrix which gets decomposed easily by sodium carbonate of fusion mixture and form soluble sodium aluminate and sodium silicate.

2.2. Characterization of untreated and treated ruby samples

Elemental characterization of both the untreated and the fusion mixture treated ruby gemstones was carried out by energy dispersive spectroscopy (EDS) of X-ray attached with field emission scanning electron microscope (FESSEM). Since chromium concentration in ruby gemstones is expected to be very low (in ppm level), it became necessary to determine the chromium concentration in both types of samples by atomic absorption spectrophotometer (AAS). For this purpose, the gemstone samples were separately ground into very fine powder.Then, 0.1 g of each sample was taken in a platinum crucible separately and mixed with 0.3 g of sodium carbonate and heated gradually at a heating rate of 10 °C/min up to 950 °C and held for 1 h at this temperature. Sodium carbonate gets fused with ruby and forms sodium aluminium carbonate and sodium aluminium silicate at such temperature. During this process Cr liberates from the matrix. The whole mixture was then dissolved in 1:1 HCl and the volume was made up to 250 ml. The solutions of both types of samples were analysed for Cr by AAS (Model:Shimadzu AA-6300).

In order to identify the inorganic phases present in the untreated and the treated ruby gemstones, phase characterization was done by X-raydiffraction (XRD) (Powder diffractometer used: XPERT' PRO PANalytical, Netherland). X-ray radiation employed was Cu $K\alpha_1$ having 0.154056 nm wavelength. The FLS-980 fluorimeter equipped with Xenon lamp as light source was used to study the photoluminescence of the treated and the untreated ruby gemstones. Optical property of the ruby gemstones was studied by recording diffused reflectance spectra (DRS) in 200–800 nm wavelength range using Cary UV–vis spectrophotometer (Varian). From the peaks identified for optical absorption in the above study, the samples were excited at 400 and 550 nm wavelength separately to obtain the emission spectra. With respect to emission wavelength, excitation spectra were recorded. X-ray photoelectron spectroscopy (XPS) (Prevac, S/N 10001, Poland) studies were carried out for surface elemental characterization to know the valence states of various elements. Laser micro Raman spectroscopy having 514 nm Ar ion laser source (Seki Technotron) was used to study the vibrational analysis of different types of bond present in the samples for more accurate phase identification.

3. Results and discussion

3.1. Elemental characterization using EDS

Luminescence property of ruby is associated with impurity elements present in it. In order to know the elemental composition of both the treated and the untreated ruby gemstones, EDS were recorded and are shown in Fig. 1. It shows that untreated sample contains Al, O, Cr besides other impurities like Si, Fe, Mg and C. When the raw ruby was heat treated at 1000 °C, peak for carbon vanished and the peak intensity of Fe and Cr were reduced due to their high dissolution in the alumina matrix. But in the case of fusion mixture treated ruby, peaks of most of the impurities such as Fe, Mg and Si were found to be absent due to their complete removal. Further, the intensities of Al, O and Cr peaks were reduced compared to the untreated sample. The concentration of Cr in the untreated, heat treated and fusion mixture treated samples determined from AAS is found to be 0.22, 0.20 and 0.05 mol% respectively. The reason for reduction of Al and Cr concentration in the ruby can be attributed to the reaction of surface layer of alumina with sodium carbonate in the fusion mixture to produce sodium aluminate and carbon dioxide.

$$Al_2O_3 + Na_2CO_3 \rightarrow 2NaAlO_2 + CO_2$$

Similarly, chromium (III) oxide present in the ruby matrix also reacts with sodium carbonate in the presence of air to produce sodium chromate and carbon dioxide.

$$2Cr_2O_3 + 4Na_2CO_3 + 3O_2 \rightarrow 4Na_2CrO_4 + 4CO_2$$