Mineralogical investigations on corundum from Hunsur area of Mysore district, Karnataka, India

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ABSTRACT:
Corundum from the Hunsur area of Mysore district is investigated with respect to its mineralogical and advanced gemological properties. Spectroscopic techniques namely, UV-Visible and Fourier Transform Infra Red (FT-IR) Spectroscopy and Scanning Electron Microscopy (SEM) along with EDAX are being utilized in the study to know the elemental configuration of the samples. The studies show predominance of Cr and Fe ions in the samples which has imparted red colour to corundum. Vibrational spectroscopic study indicates the presence of different hydroxylated ions in the crystal lattice. SEM study has revealed the presence of surface cracks and the hydroxilated form of oxides in the crystal. The studies along with chemical analysis show strong presence of associated impurity elements that have made the crystal to be opaque, diminishing its gemological value.

KEY WORDS: Corundum, Ruby, Hunsur, Cause of Colour, Spectroscopy, Scanning Electron Microscopy.

INTRODUCTION:
Corundum crystallizes in the hexagonal system with Aluminum Oxide (Al₂O₃) as the main composition. Gemstone variety of corundum show different colours. The presence of trace elements such as chromium (Cr), iron (Fe), titanium (Ti) and vanadium (V) etc [1] as impurities makes it desirable to be classified as gem varieties like ruby or sapphire. The red variety of corundum is known as ruby and that of all other colours are generally considered as sapphire. The mineralogical investigations with respect to the elemental impurities present in the crystals are essential to make a detailed study of gem minerals.

The present study is being carried out on the red variety of corundum occurring in the areas around Hunsur in Mysore district of...
Karnataka. Geological studies have been carried out in the study area to delineate the mineralized zones of gem variety corundum or rubies. The area predominantly consists of peninsular Gneiss, which has undergone extensive migmatization with varying composition from granodiorite to tonalite. Major rock formations of the area include granite, charnockite, amphibolite, metatamafites and metapelites. Pegmatite veins and dolerite dykes are the common intrusive bodies in the area [2,3]. The flat and low-lying areas covered by a thick layer of soil and laterite horizons are found to have deposits of corundum crystals. The individual crystals with well developed faces and brownish red colour are collected from the study area. These occurrences are mainly confined to the areas of contact between acidic intrusives with the ultramafic, meta ultramafic and metapelitic bodies. In this work an attempt has been made to characterise the gemstone samples from Hunsur, Karnataka using the advanced spectroscopic techniques, UV-Visible and FT-IR spectroscopic studies. SEM and EDAX.

MATERIALS AND METHODS:

Samples collected from the study area are analyzed based on its visual appearance. The samples collected from the field contain different surface impurities which are to be removed from the crystals for obtaining accurate results. The selected samples are washed in ultrasonicator bath and thereafter with mild acid to remove the gangue particles or impurities present on the surface. The samples after preliminary cleaning and acid treatment were cut into suitable size and polished to sort them based on its geological characteristics and to meet the desirable standard for carrying UV-Visible and FT-IR spectroscopic studies. UV-Visible measurement is done on Varian 5000 Spectrometer equipped with an ozone free Xenon arc lamp. IR spectra were recorded from 4000 to 400 cm\(^{-1}\) using a NICOLET Thermo scientific spectrometer. SEM is carried out using a Zeiss Scanning Electron Microscope attached with EDAX.

RESULTS AND DISCUSSIONS:
The spectra obtained for the sample using different advanced spectroscopic analyses are well observed and discussed relatively. The UV-Visible spectrum in the wavelength range of 200 nm to 600 nm is shown in figure 1. The spectrum pertaining to vibrational spectroscopic study on the sample using the Fourier Transform Infrared (FTIR) Spectroscopy in the wavelength range between 4000 cm\(^{-1}\) to 500 cm\(^{-1}\) is depicted in figure 2. Micro level high resolution images of the sample obtained using Scanning Electron Microscopy (SEM) is shown in figure 3, and figure 4 shows SEM images along with the Energy Dispersive X-ray Spectroscopy (EDAX) results.

UV-Visible Spectroscopy:
UV-Visible spectra of the sample is observed in the wavelength range of 200 to 600 nm. The peak shown by the corundum sample (Figure.1) corresponds to the presence of different essential as well as undesirable impurities in Rubies.

![Figure 1](image_url)  
**Figure 1.** Showing the absorbance peaks obtained for the corundum sample from the study area.

The spectrum shows continuous peaks in the wavelength range between 200 to 600 nm. Typical peaks observed in corundum due to Fe and Cr are at 371, 380, 401, 461, 467,475,491 and 535 nm [1,3]. The absorbance peaks seen in a wavelength range from 371 nm and up to 400 nm are mainly related to the presence of Fe\(^{3+}\) and those
observed from 401 nm to 535 nm are confined to Cr$^{3+}$ ions in the sample [1,3]. The spectra obtained in the present study shows absorbance peaks in a closely spaced nature from 350 nm to 475 nm, wherein the peaks at 371 nm and 461 nm are of considerable magnitude and, that at 401 nm is of anomalously higher magnitude. This peak at 401 nm is generally seen in Rubies due to the spin allowed transition of Cr from the ground state [4-6]. Continuous peaks of varying magnitude from 200 nm to 370 nm confirm the presence of unknown impurity elements in the crystal surface.

**FT-IR Spectroscopy:**
This method of vibrational spectroscopy works based on the principle of intermolecular vibrations seen to occur in different substances. Such vibrations are mainly due to the –OH bonds existing between the volatile molecules of study. Energy of light in the infrared spectrum is between 500 to 4000 cm$^{-1}$ and the vibrational energy of atoms and molecules also comes under this range [7]. Hence the FT-IR spectrum of the selected corundum sample is observed for a wavelength range between 500 to 4000 cm$^{-1}$. The typical absorption peaks seen in ruby at 3086, 3240, 3324 and 3418 cm$^{-1}$ [8-10] are found to be absent in the sample.

**Figure.2.** Showing the FT-IR Spectra of the corundum sample collected from the study area.

The repeated and closely spaced peaks seen at the 490 and 510 cm$^{-1}$ indicates the presence of Alumina and Iron. These peaks are very common in the natural variety of corundum and are reported from previous works [7,8]. The peaks seen in the range 500 cm$^{-1}$ to 1000 cm$^{-1}$ are mainly confined to the presence of alumina itself. Two peaks of lesser magnitude seen closely spaced at 2300 cm$^{-1}$ and 2400 cm$^{-1}$ are corresponding to the hydroxylated form of alumina. These peaks may also be due to the presence of hydrous titanium aluminium oxide as reported from other studies [8-10].

**SEM and EDAX study:**
Scanning Electron Microscopy is helpful in understanding the surface fractures and microstructures of the crystal. It has been carried out along with the EDAX to understand the presence of other mineral inclusions in the crystal lattice. The images could clearly explain about the inhomogeneity in the surface of the crystals as evident from the fractures and cracks present. The EDAX data obtained for the sample shows the presence of the elements such as Al, O, Fe, Si, C, Ti and Zn on the surface and fractures of the crystal. The presence of hydroxilated form of alumina Oxide (Figure.4) and carbonates (Figure.3) are also observed in the surface. The same can be attributed either to metamorphism or to the role of hydrothermal fluids.

Chemistry of the analyzed sample from Energy Dispersive X-ray Spectroscopy shows 98.77 wt% of Al$_2$O$_3$ and other oxides contributing only 1.23 wt%. Among the other oxides present in the crystal, Cr2O3 predominates with 0.65%, followed by Fe$_2$O$_3$, CaO, Ga$_2$O$_3$, TiO$_2$ and V$_2$O$_5$.

**Figure.3.** The SEM image of the corundum sample collected from the study area showing Carbonates.
CONCLUSION:

The study has been carried out to understand the mineral chemistry of corundum from the area around Hunsur of Mysore district, Karnataka. The spectroscopic studies on the Corundum are helpful in finding out the essential elements in ruby and in understanding the effect of undesirable impurity elements occurring as oxides and hydroxides on its gemological quality. UV-Visible spectrum shows prominent peaks in wavelengths associated with Cr ions along with those for Fe ions. Closely spaced repeated peaks of higher magnitude are seen in the sample, owing to the presence of undesirable elements in the crystal lattice, degrading its transparency and colour. FT-IR spectrum is quite typical of that of the corundum, which does not shows any considerable peak apart from that are confined to Aluminum rich hydroxylates. Such hydroxylated molecule of Al, C, Zn and Fe are observed in the SEM images obtained along with EDAX for the samples. The SEM images also show the presence of surface cracks and fractures. Presence of other oxides apart from Al₂O₃ in the crystal is ascertained to be very less from the Energy Dispersive X-ray Spectroscopic studies. Cr has imparted a bright red colour to the crystal but its transparency was affected by the excessive presence of undesirable impurities. All the above studies substantiated that the quality of the corundum from the study area is of semi precious quality ruby.

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