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Characterization of Gem and Abrasive Variety Corundum from Wyra Area of Khammam Schist Belt, Telangana, India, Using Advanced Spectroscopic Techniques

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ABSTRACT

Corundum of varying qualities occurring in association with Khammam schist belt are studied with respect to their Geochemical and Mineralogical aspects. Studies have been carried out using the advanced spectroscopic techniques namely, Photoluminescence, UV-Visible, FT-IR, Raman and EDXRF analysis. The results obtained from the studies shows the predominance of colour causing element Cr and other associated elements like, Ti, V and Ga in Red variety of corundum than the abrasive corundum crystals, while Fe is found predominant in colourless or abrasive variety. From EDXRF studies the presence of impurity ions in the crystal lattice is quantified and its effect on the corundum crystal has been ascertained.

Key Words: Corundum, Ruby, Telangana, Spectroscopy, Cause of colour

INTRODUCTION AND GEOLOGY

In and around Wyra taluk in the Khammam district of Telangana, India, occurrences of corundum of abrasive variety and rarely of gem variety are observed. The study area lies in the Khammam schist belt (KSB) which is a continuation and part of the Nellore-Khammam Schist belt (NKSB) (Ramam and Murthy, 1997).

The main lithology of the area include amphibolite, schists and gneisses of varying compositions, anorthosites, pegmatites and quartz veins, corundum bearing magnesium and aluminum rich pelitic granulites and hornblende pyroxene granulites (Ramam and Murthy, 1997; Patil, 1973). Metamorphosed pelitic, psammitic and calcareous sediments are represented by garnetiferous biotite-muscovite-kyanite-chlorite schists, kyanite and sillimanite bearing meta - pelitic schists, calc -silicate rocks, quartzites, fuchsite, and magnetite quartzite. The meta-sedimentary unit is tectonically emplaced below a metavolcanic unit made up of quartz-chlorite schists, hornblende schists and tonalitic gneisses (Ramam and Murthy,1997; Leelanandam and Narasimha,1988; Narayan and Pavanaguru, 2013).

The main host rocks for corundum in the study area are sillimanite-corundum schist and kyanite schists. These pelitic schists hosting corundum are found to be in contact with altered basic bodies or pegmatitic vein. Occurrences associated with pyroxene granulites and gneisses are also seen in some localities of the Wyra taluk. Similar Geological setups hosting corundum have been reported from the study area (Patil, 1973; Rao,1981; Narayan and Pavanaguru,2013). However, corundum crystals for the present study are obtained from placer concentrations seen to occur locally in the soil profile.

Samples of gem variety as well as abrasive variety of corundum are collected from these areas and, 2 samples of contrasting qualities are selected for studies.

MATERIALS AND METHODS

Samples collected from the study area are analyzed based on its visual appearance and it has been grouped on that

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basis. Two Corundum samples are sorted from them based on the colour and gemological quality so that, one sample is of abrasive quality with colourless nature (C1, Fig.1) where as the other one is of semi precious variety with pinkish red colour (C2, Fig.2).

Figure 1: Showing C1 sample - Natural as well as in polished form.

Figure 2: Showing C2 sample - Natural as well as in polished form.

Both the samples C1 and C2 after preliminary cleaning and acid treatment were cut into suitable size and then subjected to the following analyses namely, UV-Visible Spectroscopy, Photoluminescence spectroscopy, FT-IR Spectroscopy, Raman Spectroscopy and EDXRF studies.

RESULTS AND DISCUSSIONS

The spectra obtained for both the gem and abrasive variety samples using different advanced spectroscopic analyses are displayed with contrasting colours. The UV-Visible spectra obtained for the samples in the wavelength range of 200 nm to 600 nm and Photoluminescence peaks in the wavelength range of 600 nm to 800 nm are shown in Figure.3 and Figure.4 respectively. Vibrational Spectroscopic studies on the samples using the Fourier Transform Infrared (FTIR) Spectroscopy and the Raman Spectroscopy are discussed separately. Figure 5 and Figure 6 depicts the spectra obtained using FTIR Spectroscopy in a wavelength range between 4000 cm^{-1} to 500 cm^{-1} and Raman Spectroscopy in Raman shifts ranging from 200 cm^{-1} to 800 cm^{-1}, respectively. Results obtained from EDXRF Studies are discussed and correlated with the observations made from other Spectroscopic techniques used in the research.

UV-Visible and Photoluminescence Spectroscopy

The UV-Visible spectra of the two samples are observed in the wavelength range of 200 to 600 nm (Figure.3). The spectra show significant difference in the peaks obtained at certain wavelengths. The peaks shown by the C2 sample are of more intensity and magnitude compared to that of C1 sample, indicating the presence of certain additional elements in C2, which has favored in imparting pinkish red colour. Peaks in the range of 200 to 250 nm are more densely spaced in the C1 variety of corundum sample. A prominent peak at 241 nm is seen in C1. The hydroxylated ions present in samples correspond to absorptions in this wavelength. Such ions are hence present in higher concentration in the C1 variety.

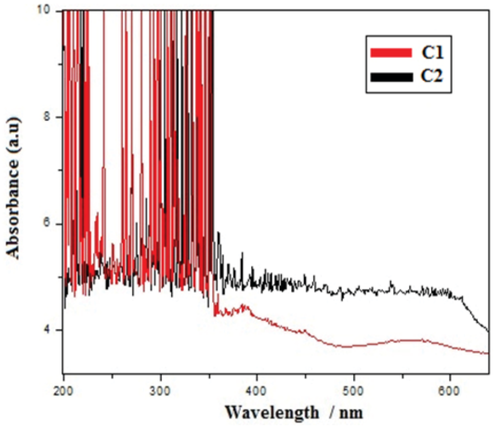

Figure 3: The UV-Vis spectra of both the samples are shown, where C1 is represented by red peaks and C2 by black colour.

Correlation of the absorbance peaks clearly shows a contrast in the peaks at wavelengths corresponding to Fe and Cr, the usual colour causing ions in ruby variety of corundum. Some of the studies (Nassau et al.,1983; Jatin and Pratima, 2015) has shown that, the wavelengths that are usually absorbed by Fe ions falls under the range of 380 to 400 nm whereas, peaks are observed to be present at 401, 461, 467, 475 and 535 nm when the Cr ions shows its prominence. In the absorbance spectra of the samples, C1 is having peaks of very minute magnitude in the wavelength range corresponding to Fe ions and it doesn't shows any absorbance in the range of Cr ions. It is identified that, the peaks in this range, corresponding to Fe and Cr are present in C2 with a comparatively appreciable magnitude, which justifies the cause of colour in the C2 sample compared to C1.

The Luminescence peaks are observed for both of the samples in an excited state at 401 nm (Figure 4). Luminescence peaks lies in the wavelength range between 600 to 800 nm. The dual peak at 692 and 694 represents the presence of Cr chromophores in both the samples (Nassau et al.,1983; Beran and Rossman et al., 2006; Jatin and Pratima, 2015).

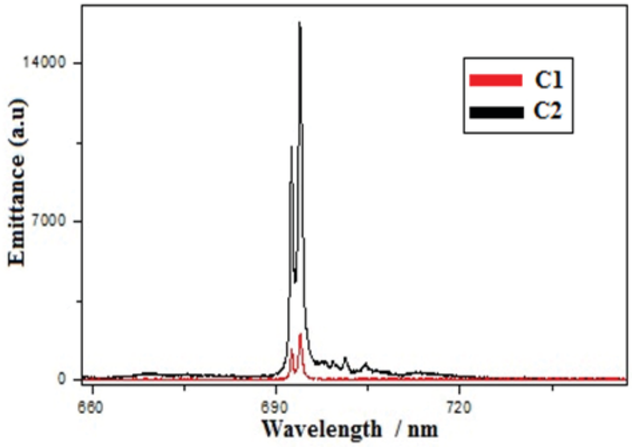

Figure 4: The luminescence spectra of both the samples are shown, where C1 is represented by red peaks and C2 by black colour.

Even though C1 sample has a significant peak at the above mentioned wavelengths, the magnitude is much lesser than that of C2. The very high magnitude of the peaks obtained for C2 samples substantiates its cause of colour due to prominent presence of Cr.

FT-IR Spectroscopy

Fourier Transform Infrared Spectroscopy or FT-IR Spectroscopy data of the samples is observed (Figure 5) in a wavelength range between 4000 cm^{-1} to 500 cm^{-1}. The spectra seen between 500 to 1000 cm^{-1} is of the same fashion with peaks at common wavelengths. Both the samples show peaks corresponding to same wavelengths, even though the C1 sample has a comparatively lesser magnitude. Therefore, these peaks are generally identified to be caused by the Alumina present in the crystal.

There are no considerable peaks seen in the C1 sample after 1000 cm^{-1}. Twin peaks observed in C2 sample at 1991 and 2100 cm^{-1}. Similar peaks are observed (Cowley, 1969; Kloprogge et al., 2004; Jatin and Pratima, 2015), indicating the presence of hydroxylated form of Alumina, corresponding to high temperature environment and the peaks seen in the wavelength range towards higher energy part is all corresponding to different hydroxylated ions in the crystal lattice. These are caused by the vibration modes related with the bending and stretching of –OH group bonds in the crystal lattice and the mineral groups that may be present cannot be always presumed to be due to the –OH association with Alumina groups. Such hydroxylated groups are similarly observed (Beran and Rossman, 2006; Kloprogge et al., 2004) to be due to the presence of other elements like Ti, Fe or V present in the crystal lattice in traces.

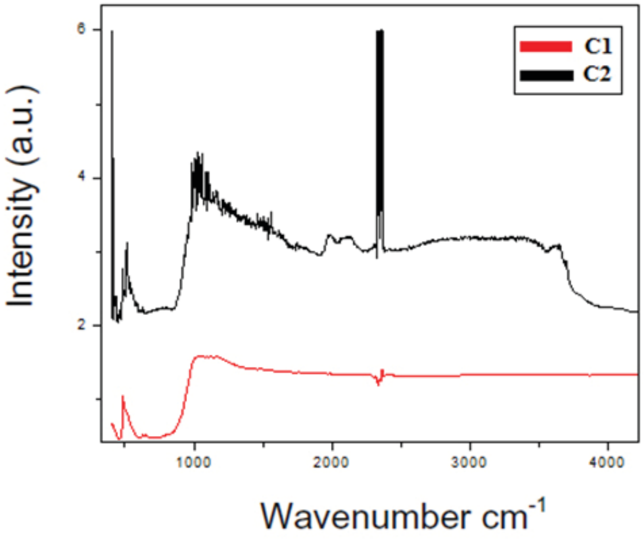

Figure 5: The FTIR spectra of both the samples are shown, where C1 is represented by red peaks and C2 by black colour.

Raman Spectroscopy

Raman spectroscopy is depended on the vibrational modes of the substances subjected to analysis. Corundum is reported to have 18 vibrational modes where 7 are Raman active, 6 are Infrared active while the rest are neither Raman nor Infrared active and unique vibrations for Corundum are usually observed at 378, 418, 432, 451, 578, 645 and 751 cm^{-1} (Porto and Krishnan, 1967; XU J-A et al., 1995; Jasinevicius, 2009). Individual spectra of both the samples C1 and C2 are well observed (Figure 6). The spectra obtained for C1 sample is devoid of any considerable peaks and is almost following a plain linear fashion.

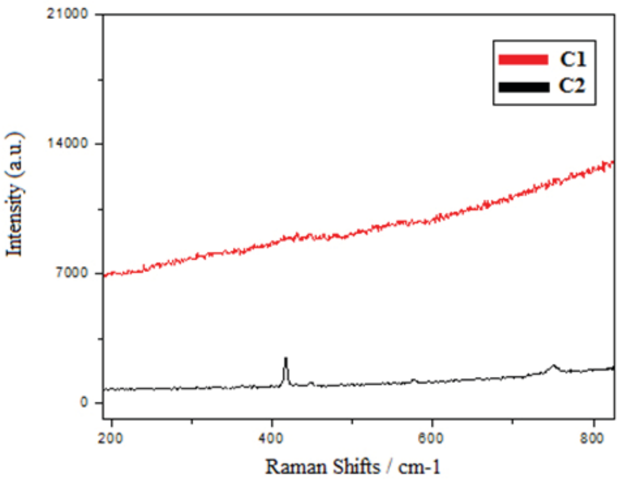

Figure 6: The Raman spectra of both the samples are shown, where C1 is represented by red colour and C2 by black.

In contrary, the spectra of C2 sample is showing a notable peak at 417 cm^{-1}, a minute peak at 750 cm^{-1} and a very minute one at 577 cm^{-1}. These peaks correspond to the typical fundamental vibrations evidenced in corundum, which are also believed to be associated with Alumina.

Geochemical Analysis

Characterization of the two variety of corundum in terms of chemical composition is highly essential in determining the cause of colour and other allied properties in Gemological perspective. The average weight percentage in terms of oxides of Al, Ca, Ti, V, Cr, Fe, Ga and Zr are obtained from the Energy Dispersive X Ray Fluorescence (EDXRF) Spectroscopy.

The presence of other oxides in the C1 samples is estimated to be within 0.8 weight percentage and the crystal is mere corundum with higher content of Al_20_3 alone, even though 0.3 weight percentage of Fe_2O_3 is also observed. The C2 sample shows 95.3 weight percentage of Al_20_3 while other oxides constitutes for an average weight percentage of 3.179 out of which, Cr_2O_3 predominates with 1.882 by weight percentage followed by, TiO_2, CaO and ZrO_2.

CONCLUSIONS

Present study indicates subtle differences in the two samples. The UV-Visible spectra shows continuous peaks in the wavelength range from 401 to 535 in the C2 sample, while it remains absent in that of C1, revealing the predominance of Cr ions in C2 sample. The emission spectra due to Photoluminescence, has prominent dual peaks in the wavelengths 692 and 694nm in C2 sample while these peaks are present in a very less magnitude in the C1 sample. This accounts to the prominence of Cr chromospheres in C2 sample. Peaks obtained from the FTIR spectra, in the higher energy level prior to 1000cm^{-1}, throws light on the existence of several hydroxylated ions in the crystal, along with Alumina in the C2 sample while, peaks in this range remains absent in C1. The Raman spectra shows peaks at the typical fundamental vibrational modes corresponding to their respective Raman Shifts cm^{-1} at 417, 750 and 577, in the C2 sample, while C1 sample is showing a spectra devoid of such peaks. EDXRF data substantiated the results obtained from other advanced spectroscopic analyses as it confirms that the presence of Cr_2O_3 and TiO_2, which are desirable constituents of quality rubies is predominant in C2 sample, while, the quantity of Fe_2O_3 is higher in C1. This study has been proven helpful in characterizing and determining the parameters and features present in the two varieties of samples collected from the study area, that are responsible for causing colour in them.

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