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RESEARCH ARTICLE

GEMMOLOGICAL APPRAISAL AND THERMO-CHEMICAL STUDY OF CORUNDUM FROM SOUTHERN KARNTAKA, INDIA, USING ADVANCED SPECTROSCOPIC TECHNIQUES

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ABSTRACT

Detrital and placer concentrations of ruby corundum of translucent, semi-translucent and opaque varieties from Bhagamandala, Hunsur and Poovanahalli respectively are studied to understand their gemmological quality. FT-IR, Raman, Photoluminescence and EDXRF analyses have been carried out on selected samples to understand the cause of colouration and geochemical control over its quality. The samples were subjected to heat treatment and its effect on the quality is analyzed using spectroscopic techniques. Thermo-chemical behavior of the samples is discussed with the help of spectroscopic studies carried out before and after heat treatment. Conspicuous peaks implying Raman active vibrational modes and chromium colour centres in the samples are perceived from Raman and Photoluminescence spectroscopy. OH- associated Vibrational modes in the corundum crystals are observed with the help of FT-IR spectroscopy showing perceptible variations with respect to their quality. The elemental abundance in the samples is discerned with the help of EDXRF studies and the concentration of conducing elements of ruby variety corundum is obtained as oxides

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INTRODUCTION

Gemstone industry is considered as an ever growing and stable industry in the world. Irrespective of changing economic scenarios, the demand for fine quality gemstones always exists unaffected. India is believed to have high potential for gemstone industry and several varieties of precious and semi-precious stones have been found and mined from different areas of the country. Among these gemstones, diamonds, rubies and sapphire are of most importance. Corundum crystallizes in the hexagonal system with Aluminum Oxide (Al2O3) as the main composition (Nassau K, 1985). Gemstone variety of corundum show different colours. The presence of trace elements such as chromium (Cr), iron (Fe), titanium (Ti) and vanadium (V) etc as impurities makes it desirable to be classified as gem varieties like ruby or sapphire (Nassau K, 1985; Nassau K, 2003; Sinha, J.K. and Mishra, P.K, 2015; Sorokina, E.S *et al*., 2015; Shyam Kumar and Shadakshara Swamy, 2017 a). Ruby variety of Corundum occurences are reported from the states of Karnataka, Tamil Nadu, Orissa, Telangana, Madhya Pradesh, Chattisgarh and Jammu & Kashmir (Indian Minerals Yearbook, 2020) and Kerala (Vidhyadharan *et al*, 2008). The availability of the best quality gemstones are rare, and most of the deposits are of lower quality with poorer colour and/or clarity which has less market value. Different kinds of treatments are in use for the enhancement of gem quality of corundum (Nassau, K, 1981; Nassau, K, 1984; Nassau, K, 1994) and heat treatment is one among them. In this study, corundum samples of three different qualities collected from Bhagamandala, Hunsur and Poovanahalli of Southern Karnataka are studied. An appraisal of gemmological quality using advanced spectrophotometric techniques is carried out in a comparative manner. Heat treatment is an the oldest methods used to improve the quality and value of rubies (NASSAU, K., 1981; Themelis, 1992; R.K. Sahoo *et al*, 2015; Manocha and Ramjibhai, 2012; Sudheendra Rao *et al*, 2016; Notari, F *et al*., 2019). An attempt is made to understand the cause of colour in each of these samples and to the thermo-chemical behavior of the samples towards hear treatment.

MATERIALS AND METHODS

This work is intended to understand the chemistry and nature of the chromophores in Ruby variety corundum of different qualities from Bhagamandala, Hunsur and Poovanahalli in Southern Karnataka, using FTIR, Raman, Photoluminescence and EDXRF studies. The individual crystals with well developed faces of the following verities namely, pinkish red translucent (R1), pale red semi translucent (R2), colourless to Dull red/flesh-coloured nearly opaque (R3) were analyzed for the study. Selected corundum crystals were polished and subjected to the above mentioned advanced Spectroscopic analyses.

Gemmological Investigations

Gemmological appraisal of corundum based on the optical and other properties need to be carried out to classify the deposits reported from different places. The basic mineralogical and gemmological properties of the samples are studied and the parameters are provided in the table. These following parameters are employed to classify the samples as shown in Table 1.

Table 1. Showing Comparative Gemmological Properties of the three Samples)

Property	Sample R 1	Sample R 2	Sample R 3
Colour	Pinkish Red	Pale red	Dull Red
Diaphaneity	translucent to semi translucent	Semi-Translucent to Opaque	Opaque
Refractive Index (R.I)	1.761 – 1.769	1.760-1.768	--
Birefringence	0.008	0.008	--
Dichroism	Red to Crimson Red	light red	--
Specific Gravity (S.G)	3.9	3.9	3.9
Hardness	9	9	9

R1 R2 R3

Fig. 1. Showing R1 (Pinkish red translucent, From Bhagamandala), R2 (Pale red semi translucent, From Hunsur) , R3 (Colourless to dull red to flesh-coloured Nearly Opaque, From Poovanahalli)

FT-IR Spectroscopy

Fourier Transform Infrared Spectroscopy or FT-IR Spectroscopy data of the samples is observed in a wavelength range between 4000 cm-1 to 500 cm-1. The spectra is of the same fashion with peaks at common wavelengths, even though the R2 sample has a lesser magnitude and the R1 and R3 sample shows very closely spaced peaks presumed due to the higher content hydrous molecules in it. Peaks of minor intensity are upto 2138 cm^{-1} in the pinkish red translucent and Pale red semi-translucent samples. These are formed due to the presence of different hydroxylated elements in the crystal. Similar peaks were reported for corundum from other locations (Beran and Rossman, 2006; Kloprogge *et al*., 2004; Jatin and Pratima, 2015). There is a cluster of peaks of high intensity seen in the wavelength range between 2330 cm^{-1} to 2350 cm^{-1}. They are normally seen in corundum indicating the presence of -OH- associated Alumina molecules (Nassau K, 1985; Nassau K, 2003).

Raman Characteristics

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; Shyam Kumar and Shadakshara Swamy, 2017). The spectra obtained for semi translucent pale red sample is of very low magnitude at 417 cm^{-1}. In contrary, the spectra of R1(pinkish red) and R3(whitish opaque) samples are showing peaks of comparatively higher magnitude at 417 cm-1, a minute peak at 645 cm−1 and very minute peaks in between this range**.** These peaks correspond to the typical fundamental vibrations evidenced in corundum, which are also believed to be associated with Alumina.

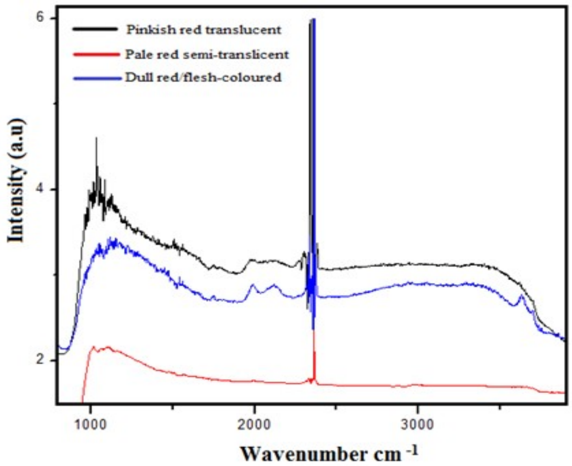


Fig. 2. FTIR spectra of the natural samples

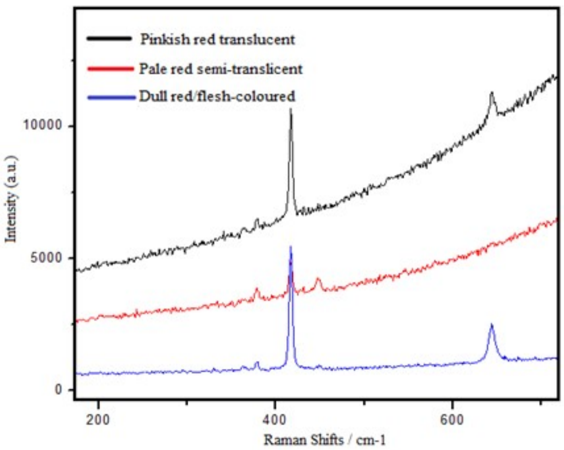


Fig. 3. Raman spectra of the natural samples

Photoluminescence Spectroscopy

The Luminescence peaks are observed for the sample in an excited state at 401 nm. 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. Similar peaks were reported for corundum from other locations (Nassau *et al*., 1985; Beran and Rossman., 2006; Jatin and Pratima, 2015; Shyam Kumar and Shadakshara Swamy, 2020). These dual peaks shows higher intensity in the pinkish red translucent variety which is twice that of the pale red semi-translucent variety. The colourless opaque variety shows a peak of very minute intensity. Despite of high Cr content in the pale red variety, the low intensity peaks of Cr chromophore indicates the dependency of the emmitence spectrum on transperancy of the crystal.

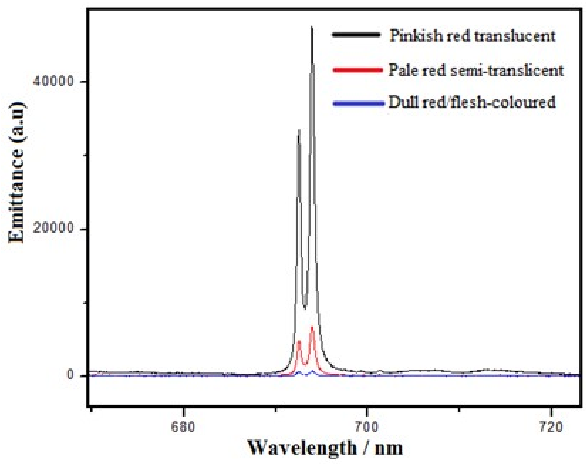


Fig. 4. Emittance spectra of the natural samples

Elemental Chemistry

The elemental chemistry of the sample is determined using Energy Dispersive X-Ray Fluorescence (EDXRF) spectroscopy. Characterization of corundum in terms of chemical composition is highly essential in determining the cause of colour and other allied properties (Vodolazov, O. and Shorokhova, A, 2021; Stone-Sundberg J.L *et al*, 2021). The average weight percentage in terms of oxides of Al, Ca, Ti, V, Cr, Fe, Ga and Zr is taken for the study. The concentration of different elements is quantified and it is Al2O3> Cr2O3> Fe2O3> CaO> V2O5= TiO2> ZrO2> Ga2O3 in the pinkish red translucent variety, Al2O3> Cr2O3> Fe2O3> CaO> V2O5> Ga2O3> TiO2> ZrO2 in the brick red semi-translucent variety and Al2O3> CaO> Fe2O3> Cr2O3> TiO2> Ga2O3> V2O5> ZrO2 in the colourless opaque variety. The weight percentage of Cr which acts as main chromophore in ruby is highest in R2 variety than in R1 and R3. R2 has highest content of Fe followed by R3 and R1.

Table 2. Showing the results obtained from EDXRF studies on the samples before treatment

Oxide	R1 (Wt%)	R2 (Wt%)	R3 (Wt%)
Al_2O_3	99.392	98.775	98.257
CaO	0.029	0.034	1.241
TiO_2	0.013	0.007	0.018
V_2O_5	0.02	0.02	0.004
Cr_2O_3	0.377	0.652	0.022
Fe_2O_3	0.143	0.488	0.447
Ga_2O_3	0.011	0.023	0.011
ZrO_2	0.016	0	0

Heating Experiment and thermo-chemical effects on the samples:

The concept of Heat Treatment or Annealing is considered to be useful in the study of Corundum which do not have true red colour but have undesirable colour tints. This brings down its value since such colour prevents categorization of these stones as rubies. The thermo-chemical properties of the Rubies are important in order to understand the possibility and methodology to be adopted for establishing a technique to improve the colour and clarity. In the present study, the Ruby sample was cleaned with mild acid to remove the undezirable gangue particles present on the surface. After cleaning the sample was subjected to heat treatment to a temperature of 800 °C for a duration of 3 hours under normal conditions.

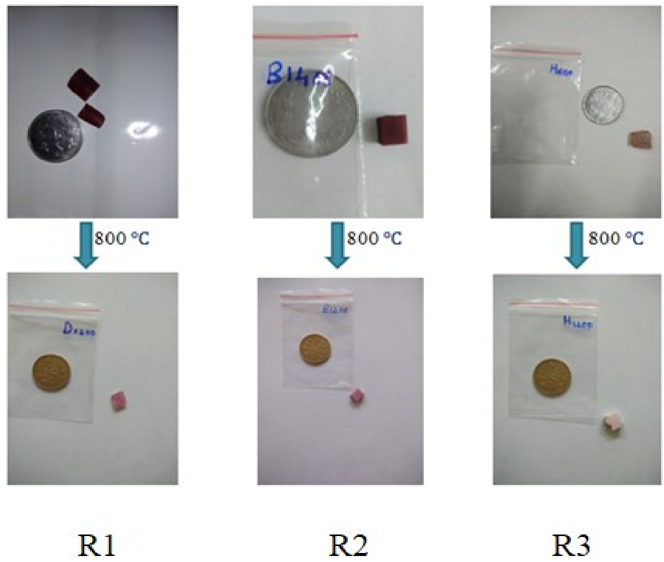


Fig. 5. Heating experimental features of R1 (Pinkish red translucent, From Bhagamandala), R2 (Pale red semi translucent, From Hunsur), R3 (Colourless to dull red to flesh-coloured Nearly Opaque, From Poovanahalli)

The heat treatment process has resulted in drastic variations in the colour and other physical properties of the corundum samples considered for the study (Mehta, B.K, 2018; Hughes, E.B; Paridieu, V *et al*., 2015; Saeseaw, S *et al*.,2018; Saeseaw, S *et al*., 2020). A general fade in colour is noticed in the samples after heat treatment. The changes resulted in physical properties are shown in Fig.2.

Spectroscopic Implications of Thermo-Chemical Effects

The spectrospic implications of heat treatment is studied with the help of FT-IE Spectroscopy, Raman Spectroscopy and photoluminescence emittance peaks.

FT-IR Spectra: There is subtle differences identified in the absorption spectra of the samples from the FTIR studies (Phlayrahan, A *et al*.,2018; Zhang, Yuyang and Meihua Chen. 2022). The overall intensity of the spectra are reduced many fold and the peaks seen closely spaced up to 2300 cm-1 due to various hydroxylated impurities are found to absent. All the three samples have maintained the peaks from 2330-2350 cm-1 which is reported to have resulted from hydrous alumina in the crystal, unique in corundum.

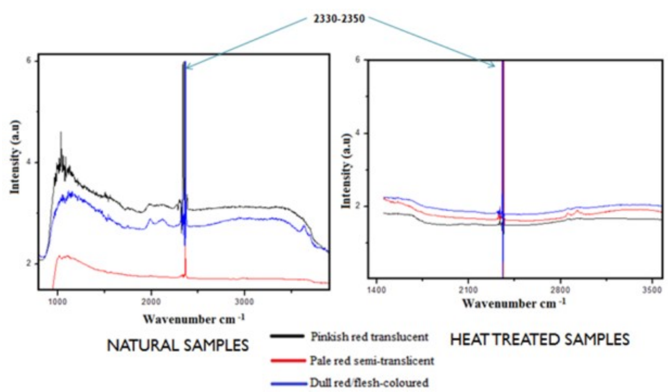
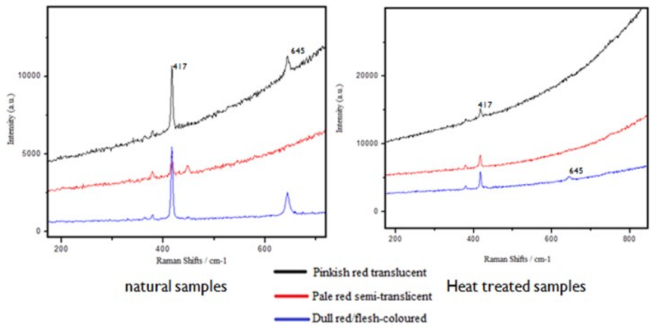


Fig. 6. Ftir spectral variation after heat treatment

Massive dehydroxylation process is evident from the spectra of the samples as a result of heat treatment Such dehydroxylation migh have happened as heat treatment causes hydrogen atoms to diffuse into the optical absorption cavity and an overall reduction in absorption peaks have resulted subsequently (Paridieu, V *et al*, 2015).

Raman Characteristics pre and Post heat treatment: Intensity of the peaks are seen to have reduced many fold. The peaks at 378cm-1 and 417 cm-1 are seen to have preserved even after heating in all the three samples. The peak at 645 cm-1 in R1 sample is found to be absent after heating. The peaks at 378cm-1, 417 cm-1 and 645 cm−1 are seen to have preserved even after heating in R3. The vibrational modes at 432 cm-1 and 645cm-1 are seen to be absent or reduced highly after heat treatment. Massive dehydroxylation process is evident from the spectra of the samples as a result of heat treatment



Fig,7. Raman Spectral variation after heat treatment

Photoluminescence Spectroscopy: Intensity of the peaks are seen to have reduced many fold. There is reverse effect seen in the comparative intensity of R1 and R2 after heat treatment.

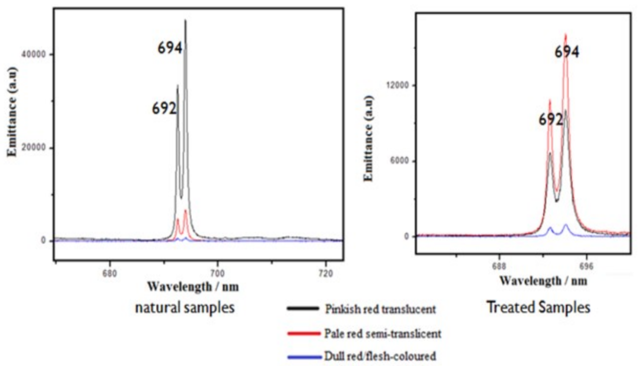


Fig. 8. Photolumescencespectral variation after heat treatment

R2 has got a magnified peak after heating due to the dissolution of OH- molecules, which had hindered the formation of emittance peaks. However, there is no difference in the intensity of peaks formed by R3 after heat treatment.

Post- Treatment Variations in Chemistry

The concentration of different elements as oxides is seen to have changed in all the three samples, as shown in Table 3 to 5. The concentration of different elements after heat treatment is quantified and it is Al2O3> Fe2O3> Cr2O3 > CaO> Ga2O3> TiO2> V2O5>ZrO2 in the pinkish red translucent variety, Al2O3> Cr2O3> Fe2O3> CaO> TiO2> V2O5 > ZrO2 = Ga2O3 in the pale red semi-translucent variety and Al2O3> CaO> Fe2O3> TiO2> Cr2O3> Ga2O3> V2O5= ZrO2 in the dull red/ flesh-coloured opaque variety. The weight percentage of Cr which acts as main chromophore in ruby is highest in R2 variety than in R1 and R3. R2 has highest content of Fe followed by R1 and R3. The weight percentage of Cr and Fe is seen to have increased in the R2 and R3 samples. In contrary the Pinkish red variety shows a reduction in the Cr wt% and an increase in the Fe wt%.

Tabe.3. Showing the changes in chemistry of the samples from Bhagamandala area of Kodagu district, Karnataka, after heat treatment

Oxide	Wt %	Wt %
	Natural	Heated at 800 °C
Al_2O_3	99.392	99.12
CaO	0.029	0.16
TiO_2	0.013	0.01
V_2O_5	0.02	0.01
Cr_2O_3	0.377	0.23
Fe_2O_3	0.143	0.45
Ga_2O_3	0.011	0.01
ZrO_2	0.016	0.01

Tabe.4. Showing the changes in chemistry of the samples from Bhagamandala area of Kodagu district, Karnataka, after heat treatment

Oxide	Wt %	Wt %
	Natural	Heated at 800 °C
Al_2O_3	98.775	98.37
CaO	0.034	0.22
TiO_2	0.007	0.04
V_2O_5	0.02	0.02
Cr_2O_3	0.652	0.76
Fe_2O_3	0.488	0.58
Ga_2O_3	0.023	0.01
ZrO_2	0	0

Table 5. Showing the changes in chemistry of the samples from Hunsur area of Mysore district, Karnataka, after heat treatment

Oxide	Wt %	Wt %
	Natural	Heated at 800 °C
Al_2O_3	98.257	98.71
CaO	1.241	0.101
TiO_2	0.018	0.002
V_2O_5	0.004	0
Cr_2O_3	0.022	0.029
Fe_2O_3	0.447	0.387
Ga_2O_3	0.011	0.003
ZrO_2	0	0

CONCLUSIONS

The present study helped in understanding the nature and influence of essential and undesirable elements occurring as oxides and hydroxides on the quality of ruby corundum. Gemmological studies based on the optical properties of the samples are deployed to categorize them as of different qualities namely, semi-precious, non precious and abrasive. Presence of different hydroxylated molecules in the samples that hinders the transparency is identified using FT-IR Spectroscopy. Raman and Emittance Table.11. Showing the changes in chemistry of the samples from Poovanahalli area of Mysore district, Karnataka, after heat treatment spectrum of the samples clearly indicate strong presence of Cr as Chromophore in the samples. Low intensity peaks of Cr in the pale red variety despite of its high Cr content might have resulted due to the excessive amount of hydroxyl molecules in the crystal.

EDXRF data is used to quantify the exact concentration of different elements present in the crystal to understand the nature of vaibrational and emittance spectra. Colouration in the samples are understood to have influenced by the Cr and Fe ions present in the crystal lattice and the presence of hydroxylated elements affects on the diaphaneity of the crystals.

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