

Comparative study of the electronic structure of natural and synthetic rubies using XAFS and EDAX analyses

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Abstract. We have studied the Cr–K-edge XANES and EXAFS in natural Indian rubies from two sources and a synthetic ruby at ESRF. Weight % of various constituents in them is determined using EDAX measurements. Taking the results from the three techniques together we are able to demonstrate their feasibility in quantitative study of precious stones.

Keywords. XANES; EXAFS; Cr–K-edge; natural and synthetic rubies.

1. Introduction

Ruby belongs to the corundum class of crystals having the chemical formula, Al_2O_3 . Corundum in purest form is colourless, rare and having tetragonal structure. The oxygen atoms lie on planes in nearly hexagonal closed packed configuration with their cations between these planes in octahedral coordination. For every three octahedra, two distorted cations are occupied by an aluminum atom in an orderly arrangement; thus each aluminum atom is surrounded by six oxygen atoms.

The same corundum structure is seen in Cr_2O_3 , V_2O_3 , Ti_2O_3 , Fe_2O_3 etc. Some of these when mixed with Al_2O_3 , whereby the position of Al atom in the lattice is replaced by Cr^{+3} , V^{+3} , Ti^{+3} , Fe^{+3} ions.

When Al atom is replaced by Cr atom the red colour ruby results (Hughes 1997).

Transition metal causes colour because of their unpaired electrons and variable valence. Ruby occurs as mineral in a wide variety of quality spread all over the world e.g. Burma, India, Thailand, Nigeria, Sri Lanka, Kenya, etc. Synthetic ruby due to the low cost mass production is also available. Therefore, there is a commercial demand to distinguish a precious natural ruby from the artificial (synthetic) ruby. Some of the known methods for identification of gemstones utilize the knowledge of refractive index (RI), specific gravity (SG), double refraction (DR), hardness, colour, luster, spark and appearance (Read 1997). To determine chemical composition, techniques like spectrophotometry, Fourier trans-

form infrared (FTIR), nuclear magnetic resonance (NMR), X-ray diffraction (XRD) and trace element analysis etc are also employed (Moroz *et al* 1999). In many cases, however, these methods are not adequate, as the synthetic rubies resemble the natural one very closely in physical properties as well as in chemical composition. Since elemental contents in natural rubies also vary from one source to another (Muhlmeister *et al* 1998), it is always difficult to know precisely the exact difference in composition of natural and synthetic rubies. None of the conventional techniques can provide exact compositional data due to presence of many elements in a gem in traces. These impurities although present in traces but may sometimes greatly influence the appearance of gems.

X-ray absorption spectroscopy is a powerful and versatile technique in study of electronic structure and near-neighbour environment around a given cation. Further, being a microscopic probe, it measures the local density of unoccupied state of a particular symmetry. The position and the shape of the pre-peak, the absorption edge, the principal absorption maximum (PAM) and the other features in the XANES region give reliable information about valence state of absorbing ion and symmetry of surrounding near neighbours (Azaroff and Pease 1974). EXAFS, on the other hand, provides structural information on the local atomic environment of the absorbing species (Durham *et al* 1982).

2. Experimental

Samples studied in this paper—natural rubies, are from two different Indian sources (Karnataka and Madhya

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Pradesh) and synthetic ruby is from Verneuil's flame fusion process. The samples studied were provided by the Gem Testing Laboratory, Jaipur.

In our present study we report the results of our investigations on the comparative study of the electronic structure of synthetic (flame fusion) and natural rubies from two different Indian sources (Madhya Pradesh and Karnataka).

First of all, to find out the weight % of various atomic components on the surface of these systems non destructively, energy dispersive X-ray analysis (EDAX) was done on these at CEERI, Pilani.

The XAFS measurements were performed at ESRF, France, at beamline BM32 using high intensity and a highly polarized synchrotron radiation beam. We have recorded all the spectra at room temperature over a wide range of energy. The flux of sample was $\sim 10^{11}$ photons per second, large number of high-resolution scans were taken in each case at the beam current of ~ 90 – 100 mA. Detection was carried out in fluorescence mode in air using Si diode pairs oriented toward the sample. The fluorescence technique involves the measurement of the fluorescence radiation (over some solid angle) at right angle to the incident beam.

EXAFS analysis has been done using the ATOMS 3.0, FEFF 8.0 and UWXAFS 3.0 program packages (Rehr *et al* 1992; Stern 1993; Raval *et al* 1995).

The absorption edge was determined by the first derivative of first rise at the XAFS spectrum after pre-edge baseline subtraction. The isolated EXAFS was normalized to the edge step and converted to wave number scale by AUTOBK program. The Fourier transform was performed on k^3 -weighted EXAFS oscillation in the range 3 to 10.50 \AA^{-1} using a Hanning window sills by FEFFIT program. FEFFIT combines and modifies the EXAFS from a set of feffnnnn.dat files to the best-fit experimental chi (k) data. The fit is performed on data in k , R -space as fitting in R -space gives the most satisfactory results.

Table 1. EDAX: Natural (Indian) and synthetic (flame fusion) ruby in weight %.

Constituents	Ruby samples		
	Nat. India MP	Nat. India Karnataka	Synthetic (flame fusion)
Na ₂ O	0.020	0.025	0.020
MgO	0.20	0.21	–
Al ₂ O ₃	74.65	75.21	97.23
SiO ₂	3.43	3.35	0.52
CaO	0.032	0.005	–
TiO ₂	0.016	0.02	0.01
V ₂ O ₅	0.0051	0.01	–
Cr ₂ O ₃	0.56	0.62	0.76
Fe ₂ O ₃	1.13	1.53	0.07
Others	19.966	19.44	1.39

3. Results and discussion

We discuss the XANES and EXAFS results along with those obtained from EDAX. EDAX measurements are given in table 1 and show the main impurities present in the three samples. At a glance, it shows that the Cr content is highest in synthetic ruby followed by the natural sample from Karnataka and MP in that order. Now we turn our attention to the XANES results.

3.1 XANES at the Cr-K-edge

Figures 1 and 2 show the pre-peak and the Cr-K-edge XANES spectra for the two rubies from Indian sources (Madhya Pradesh and Karnataka) and a synthetic ruby (flame fusion), respectively.

The pre-edge peak (figure 1) has been associated mainly with the direct quadrupole transition $1s$ to the empty Cr $3d$ states (Rehr *et al* 1992; Booth *et al* 1998).

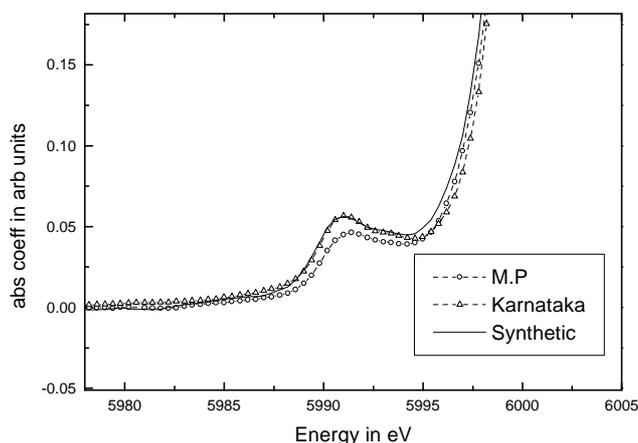


Figure 1. The Cr-K-pre-edge peak spectra for natural Indian (MP and Karnataka) and synthetic (flame fusion) rubies.

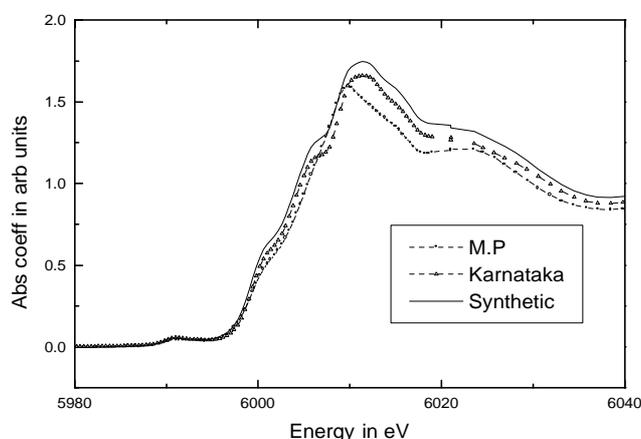


Figure 2. The Cr-K-edge for XANES spectra for natural Indian (MP and Karnataka) and synthetic (flame fusion) rubies.

This feature represents the transition probability of the Cr $1s$ electron into empty t_{2g} and e_g states that are born of Cr $3d$ and O $2p$ states under the influence of the octahedral ligand field (Rehr *et al* 1992; Stern 1993). This crystal field splits the $3d$ states into t_{2g} and e_g bands with a separation of ~ 1.79 eV (Goldman *et al* 1981). The transition probability thus also depends upon how much chromium replaces aluminum at tetrahedral site. The intensity of pre-peak also depends on the density of d states. The intensity of the pre-peak is high in natural ruby from Karnataka and synthetic ruby and low in the natural ruby from MP which is in agreement with the Cr content in these (table 1).

The position of pre-edge peak (figure 1) is more or less at the same energy of ~ 5991.00 eV in all the samples as $3d$ level is a core level and is unaffected by the outside environment.

The position of the absorption edge as determined by the first derivative of the spectra is found to be the same at ~ 5999.4 eV for all the three rubies.

Some other features are also observed just before and after the principal absorption maximum due to shake-in and shake-off structures when a second electron is ejected rather than excited. The partition of kinetic energy between the two ejected electrons shows up as a step followed by the continuum, instead of peaks.

Now we come to the main peak (figure 2), known as principal absorption maximum (PAM), arising due to $1s \rightarrow 4p$ dipole transition. The position of the main peak (PAM) also shows the valence of the absorbing ion. The PAM is found at 6011.38 eV for the Indian ruby from Karnataka and the synthetic ruby (flame fusion) and at 6009.78 eV for the Indian ruby from MP. This indicates that the effective valence of Cr is less in case of ruby from MP than the two other samples. The intensity of main peak (PAM) depends upon partial density of $4p$ states (Azaroff and Pease 1974). The density of the $4p$ states is highest in synthetic ruby followed by the Karnata

taka ruby and the MP ruby in the same order as Cr_2O_3 contents (table 1).

The XANES features from multiple scattering afterwards are almost same as the crystal structure of all the samples and the plane of measurements is the same.

3.2 The Cr-K-edge EXAFS

Figure 3 represents the k^3 weighted experimental and fitted Fourier transformed $c(k)$ spectra in r space and figure 4 represents the filtered back Fourier transformed $k^3c(k)$ vs k (\AA^{-1}) spectra for the natural and synthetic rubies.

The EXAFS fitting has been done for only first two shells from 1.25 \AA to 2.9 \AA in r -space, as the system is too complex and the information on site geometry of most impurities is unknown to permit any reliable analysis for the higher shells. The first two shells in the r -space were fit then back-Fourier transformed (figure 4). The agreement between experimental curves and fitting is quite nice. The Cr-O distance and coordination numbers for each shell and other structural factors such as Debye Waller factor, S^2 , and amplitude reduction factor, S02 for the fittings are shown in table 2.

The EXAFS (table 2) clearly shows that there are two distances for the first shell. The Cr-O(1) shorter distance pertains to Cr replacing Al at the tetrahedral sites and the longer Cr-O(2) distance to replacing Al at octahedral sites. The S02 and DW factors for all the fittings are quite reasonable vindicating the good quality of fittings. The amount of Cr at the tetrahedral site is maximum in the Karnataka ruby and a little less in the case of synthetic ruby while it is substantially less in case of MP ruby. This would imply larger transition probability for the $1s-3d$ pre-peak in case of Karnataka and synthetic ruby and a smaller probability in the MP ruby. This is exactly what we observed by the way of intensity of pre-peak in

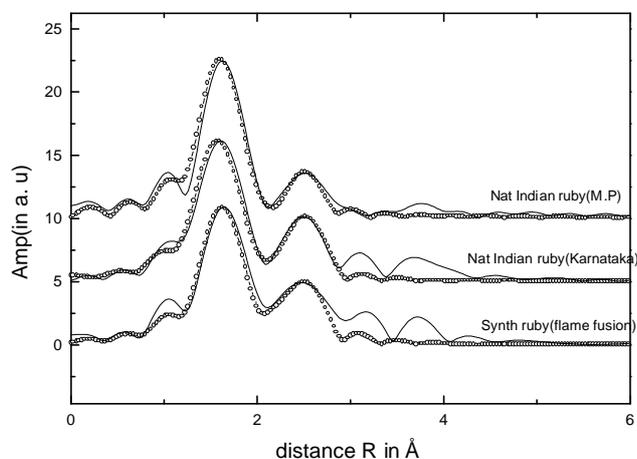


Figure 3. The k^3 -weighted Fourier transformed spectra {exp. (—) and fitted (circle)} for natural and synthetic rubies.

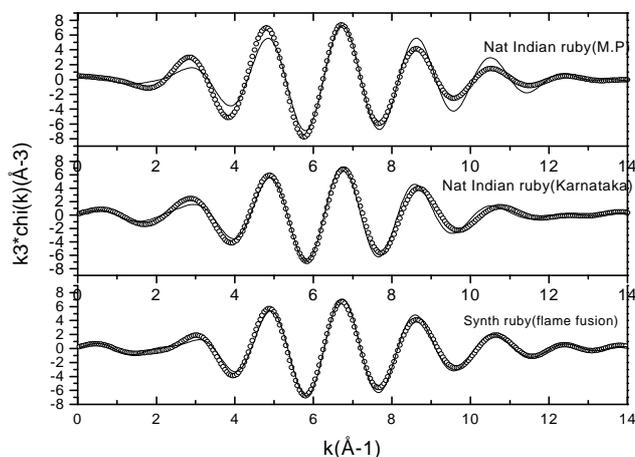


Figure 4. The k^3 -weighted filtered $c(k)$ vs k spectra {exp. (—) and fitted (o)} for natural and synthetic rubies.

Table 2. Values of Cr–O distance and other structural parameters obtained from the EXAFS analysis for first shell fittings.

Ruby sample	Tetrahedral site		Octahedral site		Amp. red. factor S_0^2	D–W factor s^2 (\AA^2)
	Cr–O(1) (\AA)	Cr–O(1) (n1)	Cr–O(2) (\AA)	Cr–O(1) (n2)		
Nat. Ind. (MP)	1.95	2.49	2.06	3.00	0.716	0.0008
Nat. Ind. (Karnataka)	1.92	3.0	2.04	2.95	0.756	0.0008
Syn. (flame fusion)	1.94	2.95	2.06	3.00	0.726	0.0008

figure 1. Further, a glance at table 1 shows that Cr content is maximum in the synthetic case followed by Karnataka and MP ruby in that order. Since intensity of a transition is proportional to both transition probability and density of states, these results would predict higher intensities of the pre-peaks in synthetic and the Karnataka rubies and a lower intensity in case of MP ruby. This is exactly what we observed in figure 1.

4. Conclusions

We have made EDAX, XANES and EXAFS measurements (Cr–K-edge) on three ruby crystals from different sources, two natural and one synthetic. EDAX gives us the Cr content and concentrations of other impurities in them. From XANES and EXAFS we are able to quantitatively estimate the Cr–O distances and Cr population at the octahedral and tetrahedral sites. The results from three measurements show very good agreement and taking all of them together we are able to successfully demonstrate how these techniques can be used in study of the precious stones.

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