| ESRF | **Experiment title:** Study of Chemical State and Local Geometry of the Impurity Atoms in Rubies | **Experiment number**: CH1312 |
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**Names and affiliations of applicants** (* indicates experimentalists):

***Naurang L. SAINI**

*Krishna B. GARG

Jean Louis HAZEMANN

Dinesh Mohan BHARDWAJ

Pushpa PAREEKH

*Gaetano CAMPI

*Claudia DEL'OMO


## Report:

The proposed work was focussed on a study of the chemical states and the local geometry of the 3d impurity ions, responsible for colors in the ruby. The aim was to make a systematic investigation on the natural rubies from different mines and synthetic ones grown by different processes. During the assigned beamtime, high resolution polarised XANES and high quality EXAFS data were collected at the Cr K-edge in thirteen corundum single crystals on the pinnacoidal [0001] face with fluorescence detection at room temperature. These crystals came from different mines in India, Africa, Myanmar and South America. Some of these were irradiated on one of the two opposite polished faces with Ni and Fe ions of a few Mev energy with different fluence values at Nuclear Science Facility, New Delhi. A few of them were subjected to heat treatment- different temperatures, heating and cooling cycles and for different periods of time. In most cases the irradiation or heat treatment is seen to induce significant changes in the colour, lustre and transparency of the crystals which, in fact, was intended. Untreated crystals were also measured on identical faces for reference.

A preliminary analysis of the data has shown significant changes in the XANES part in the treated samples (see fig. 1 for a a non-treated Rub4S15 and fig. 2 for an irradiated ruby crystal Ruin3S14) pointing

to change in chemical state of the Cr cation and its local bonding. Also, the EXAFS part appears to show some minor variations implying some minor changes in the n-n environment of the Cr cations.

The difficult part is, however, to correlate the observed changes in the XANES and EXAFS spectra with the changes in colour, transparency and lustre etc. induced in the crystals by various irradiation and heating cycles. This would, however, be taken up only after a detailed analysis of the experimental data (in progress at present) is carried out. The results are to be published.

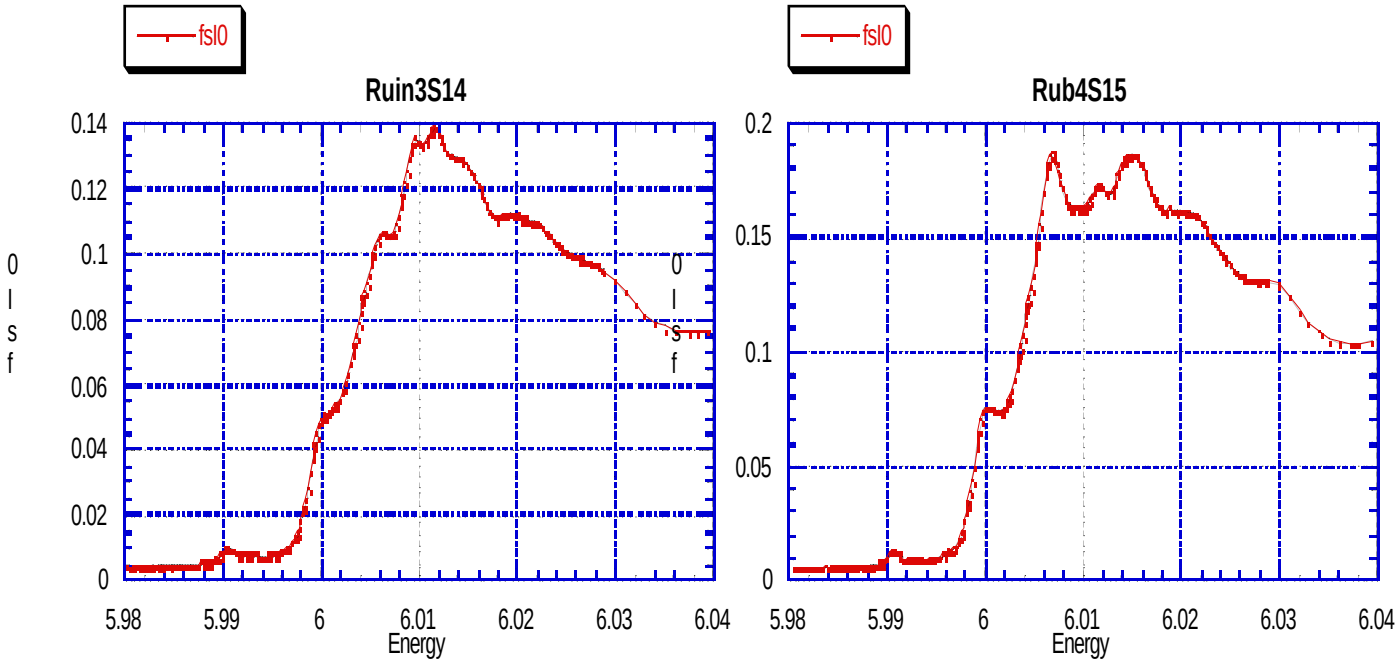


Fig. 1. High resolution Cr K-edge XANES spectra masured on a non-treated ruby (right, denoted by Rub4S15) and an irradiated ruby (left, denoted by Ruin3S14). The high resolution polarised XANES spectra were collected with the plane polarization parallel to the pinnacoidal [0001] face with fluorescence detection at room temperature.

It may be of interest to state here that subjecting gemstones to various treatments for improving their gem qualities has been going on for a long time. However, most of this kind of work has been purely empirical in nature and no serious efforts made to evolve an understanding of the mechanism that brings about such changes. Our emphasis is on this part. It may further be relevant to state here that the earlier efforts of this nature have, almost all, pointed to the valence state of Cr changing from 3+ to 2+ and 4+ in corundums doped with a very low amount of Cr impurity. Moreover, the latter has been shown to account for the thermolumioniscence and optical spectra in about 50 lattice constants.

Due to insufficient time, the measurements were performed only at the Cr K-edge. The measurements of the chemical state and the local geometry of other impurity atoms are due to attain the objectives of the propsed work on the relation between the local geometry, the oxidation state of the colour ceneters due to differen 3d impurity ions in the rubies.