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Integrated Scanning Electron Microscopy-Micro Raman spectrometer (SEM-Raman): future tool for planetary exploration

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Abstract

We identify and characterize the rock forming mineral using a newly installed, state of the art Scanning Electron Microscope integrated with Micro-Raman Spectrometer (SEM-Raman) at Physical Research Laboratory, Ahmedabad, India. The characteristic raman shifts (wave numbers) enable us acquiring the structural information and chemical fingerprint for any rock forming mineral. Due to capability of micron size sample analytical area, the unique SEM-Raman is also likely very useful for future planetary exploration for capable of analyzing the planetary materials (minerals, soils, etc) to understand the degree of crystallinity, unit cell information and also efficient in capable of scan the structural and compositional variants, e.g. the presence of different cations in different sites including the coordination configuration.

1. Introduction

Micro Raman spectroscopy is one of the powerful techniques for characterisation of Earth and planetary materials. Until now, Raman spectrometer has never been flown for planetary exploration except for NASA led Mars 2020 rover, which has planned to fly the UV Raman spectrometer to explore the martian surface with the aim for fine scale detection of minerals, organic molecules and potential biosignatures.

The motivation of studying the chromite include chromite is generally common in mantle derived ultramafic rocks also remotely detected in Moon and Martian surface or even in the meteorites. Based on possible target of planetary analogy, we have collected chromites from the ultramafic rocks from Nidar ophiolite complex exposed along the Indus Suture Zone of higher Himalaya [1]. This place is ideal for comparative planetology as the entire mantle sequence has been well exposed with variegated lower crustal and mantle units. In this short communication, we examine chromite mineral under Raman spectrometer as a utility tool to acquire the mineralogical and structural information.

2. Micro Raman Spectroscopy

The chromite sample was prepared using epoxy mound on a borosilicate glass slide which was earlier used for petrographic study. A few homogenous, smooth and clean areas are selected under Scanning Electron Microscope (SEM) (model JEOL IT300). The SEM is integrated with HybriScan Molecular Microscope (HSCMM_21) from HybriScan Technologies B.V. The Raman spectral signals are collected within the range 280 cm^{-1} to 2400 cm^{-1} with a spectral resolution better than 5 cm^{-1} Raman shift. The HSCMM_21 is a dispersive Raman micro spectrometer based on a 785 nm diode laser and back-thinned CCD detector. A scan stage with a fast 25 nm step resolution enables Raman imaging of user-defined areas. The optical microscope objective in the HSCMM_21 is designed for a vacuum environment and optimized for Raman light scattering. The light collection strength or numerical aperture is 0.65 and the spatial resolution of the confocal Raman micro-spectrometer is 1 µm in the lateral direction and 6 µm in the axial direction (for transparent materials). The Raman hyperspectral images are generated with 30 mW, 785 nm excitation, 1s exposure time. Measurements were taken on a 1 µm grid. A total number of 5508 spectra were acquired for raman analyses and finally yield the single average spectra (Fig.1).

3. Results & Discussion

There are five Raman-active vibrational modes in spinel $A_{1g}+E_g+3F_{2g}$ [2]. The three F_{2g} are often assigned as $F_{2g}(1)$, $F_{2g}(2)$ and $F_{2g}(3)$ whereas $F_{2g}(1)$ and $F_{2g}(3)$ correspond to the lowest and the highest Raman wave numbers respectively (Fig.2). The most strong band observations are common in the regions between 400-500 and 700-800 cm^{-1}. These two modes are assigned to E_g and A_{1g} modes, respectively. The bands around 200-300 cm^{-1}, 480-520 cm^{-1} and

600 cm^{-1} are diagnostic for first, second and third F_{2g} symmetry species.

In this study, the A_{1g} mode at ~685 cm^{-1} appears the strongest and well-defined mode with a shoulder near 650 cm^{-1} correspond to F_{2g} symmetry, followed by $F_{2g}(2)$ ~520 cm^{-1}(Fig. 2). The other peaks e.g. 446 and 610 $cm^{-1}$are rather weak, poorly defined and belong to E_g and F_{2g} respectively. We could observe that the most prominent the 685cm^{-1} which [1] is produced by the bonds of (Cr^{3+}, Fe^{3+}, Al^{3+})O_6 octahedra is present sample (Fig.3). The correlation between A_{1g} and chromite chemical composition can be expressed as polynomial function [3]. Using this correlation, our chromite data find a very good match with the EPMA data [4].

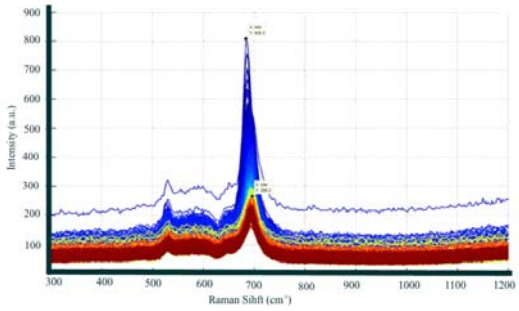

Figure 1: Spectra generated from a Raman spectral image. 1s per spectrum, 30 mW @785 nm excitation. The shift in the band around 685 cm^{-1} is obvious.

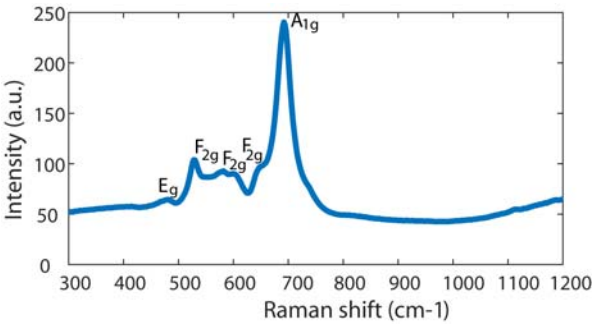

Figure 2: Identification of Raman bands with proper band assignment.

4. Summary and Conclusions

In summary, we find that the integrated SEM-Raman system is very useful for identification and characterisation of chromite. Further our results are consistent with the observed chemical composition and the vibration mode of $A^{3+}O_6$ (A=Al^{3+}, Cr^{3+}, Fe^{3+}),

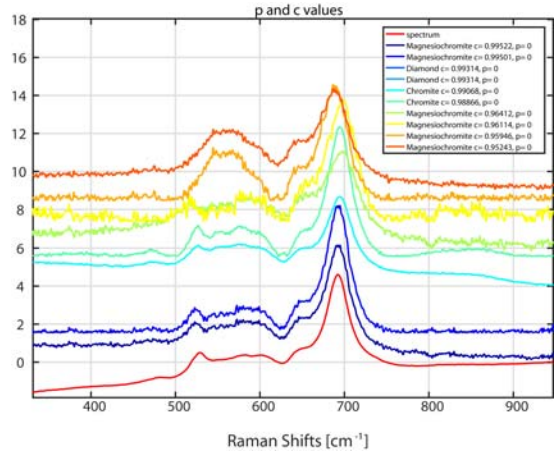

Fig. 3 Magnesiochromite as most likely or chromite after cluster average analysis and comparison with mineral database. The identification as diamond should be ignored as it is based on overlapping spectral regions without any features.

is likely the major contributor to the Raman peak of chromite. Thus, the raman peak also could be a useful guide to infer the chemical composition. Using micro Raman one can detect microbial extinct or extant life beyond the Earth vis-a-vis the planetary habitability.

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