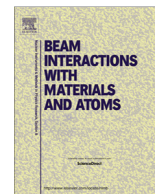




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Ion beam radiation effects on natural halite crystals

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ABSTRACT

Halites are one of the interesting material due to its color variations. Natural halites whose color ranges from transparent to dark blue were studied by UV–VIS and Raman spectroscopy. The halite crystals were irradiated with 3 MeV proton micro-beam ($\sim 20 \mu\text{m}$ beam width with $\sim 80 \text{ PA}$ beam current) for 10 and 90 min to study the radiation damage. After 10 mins of irradiation, small spot developed on the surface of transparent halite crystal whereas after 90 mins of irradiation the spot spread inside the bulk leading to a brown coloration ($20 \mu\text{m}$ initial size to $\sim 2.0 \text{ mm}$ final size). The irradiated portion and the un-irradiated portion of the halites was characterized by Raman spectroscopic technique. The variation in the population density was observed from the UV–Vis spectra. The change in the Raman band intensities was observed for transparent, blue colored and proton beam irradiation halites. Such variation of spectroscopic characteristics due to proton irradiation suggests that the halite can be used for the radiation monitoring.

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1. Introduction

Color halites are not commonly available in nature. Even though it was observed in several places in the world, the explanations for the colorization were not fully addressed. In recent years, the detailed studies on the blue halite were carried out in several places especially on Klodawa salt dome (Poland) where one can easily find the colored halites more than 12 meter accumulation [1,2]. Numerous reasons were discussed by various scientists for the colorization of minerals based on the inter valence charge transfer, molecular orbital transitions, defects, due to cationic impurities and also with the radiation effects of X-ray or gamma rays [3–6]. The presence of impurities within the halite is in all probability due to cationic substitution of Na^+ by K^+ . The variation in the color depends on the amount of impurities present in the crystal [7,8]. In the case of blue halites, defect based mechanism known as color centers is being suggested which consists of an

isolated electron or ion trapped in a defect hole. The trapped electron or ion could be able to occupy series of energy levels which partially match the energies of visible spectrum range. Thermal energy might be used to promote the trapped electrons or ions to other defect sites. One of the reason for the variation from blue color to violet color in halite crystal could be due to the emplacement of various colloidal matter into the defects present in the crystal lattice. The most common root for the blue color variation in halite crystal is the stoichiometric change in the crystal which is the results from the excess of metallic sodium within the halite crystal lattice. Even though several explanations were given on the colorization on blue halites, the formation of color on halites due to radiation effects, which could change the color of halite crystal is still being debated. Blue color formation on halite can be easily achieved by providing excess sodium vapor. Both the above mentioned processes were done in the laboratory scale by different methods such as providing excess sodium vapor; by electric spark irradiation; by ultraviolet irradiation and by irradiation using gamma ray as well as beta ray source [9–14]. Artificial color formation on halites has been attempted with gamma radiation and it was reported that the blue color forms only at 100°C whereas the brown color was formed at lower temperature nearly around

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35 °C. It was reported for this case that the color formation is due to the result of stress and the strain which are affecting the crystal lattice of halite [15].

In this work, the spectroscopic characterization results on naturally colored and colorization due to MeV ion irradiation are discussed. By obtaining a proper understanding of these crystals colorization with irradiation, there is a possibility of using these natural crystals as radiation monitors.

Proton beam irradiation effects on halites is not a focused research till date as not much efforts are made to understand the defect formation and use these crystals as radiation monitors. The formation of color centers by proton beam irradiation depends on the amount of dose (fluence), dose rate, surrounding temperature, amount of strain and the distribution of impurities, if any present in the halite crystal, etc. [16]. Gmelin et al. [1,17] argued that the radiation may not be the exact reason for the change in color since the natural halite shows thermo-luminescence, whereas the artificial halite did not show the same [1,17]. MeV energetic Proton microbeam irradiation measurements were carried out to study the effect of spatial spreading of the defects in the transparent crystals. A detailed study on how the color centers spread would be planned for future, with a focus on in-situ transmission electron microscopy studies.

2. Experimental

Solid natural halite crystals were collected from rock salt deposits in Morleben, Germany. The Fig. 1 shows the photographic image of the halite crystals used for the optical characterization and proton beam irradiation.

For the irradiation experiments, transparent halite crystal (shown in Fig. 1) was placed on the ladder with conducting carbon tape. For the ion irradiation experiment, 3.0 MeV proton beam was produced with the 9SDH-2 NEC tandem accelerator facility available at ion beam laboratory, Institute of Physics, Bhubaneswar, India. The proton beam was focused to $\sim 20 \mu\text{m}$ width square size beam spot utilizing two sets of 4-way precision micro-slits and a set of quadrupole doublet focusing magnet system available with the micro-beam line of the tandem accelerator [18]. The target stage is mounted on an X-Y stepper table with $0.6 \mu\text{m}$ stepping resolution. The $20 \mu\text{m}$ width proton beams were allowed to fall on the halite crystal for 10 min and 90 min at different places on the transparent white halite samples. The beam current was maintained at $\sim 80 \text{ pA}$. The equivalent fluence for 10 min and 90 min proton irradiation was calculated to be 7.50×10^{16} protons/cm² and 6.75×10^{17} protons/cm² respectively. Surface morphology of the samples was characterized by an environmental scanning electron microscopy (ESEM) (FEI Quanta 250) with an accelerating voltage of 1 kV. Micro-Raman spectroscopy measurement was done with 1.50 mm spot size, 0.8 mW laser power and 20 s accumulation time. The spectroscopic properties were studied using

Shimadzu UV-3101PC- UV Vis Spectrometer. The vibrational properties were analyzed using the micro-Raman spectrometer (Lab-Ram HR Evolution, Horiba) with 532 nm Nd-YAG laser.

3. Results and discussion

The UV-Vis spectroscopic analysis was carried out to observe the change in the optical absorption band due to the variation in the color center. Fig. 2 show the UV-Vis spectra of the transparent and blue colored halites. The transparent halite sample (Sample A) didn't give any optical absorption peak as expected, whereas the other colored halite crystals, viz., Sample C, E and G (for samples, refer Fig. 1) showed the absorption band peak around $594.7 \pm 0.2 \text{ nm}$, $585.1 \pm 0.7 \text{ nm}$, $596.6 \pm 0.5 \text{ nm}$ with FWHM as 105, 105 and 110 nm, respectively (for UV absorbance spectra, data shown in Fig. 2). The absorption peak was found to be sharper for Sample C and Sample D, much broader for Sample G. Based on the absorption band, we could be able to understand the types of defects present in the halite crystals. Various types of bands such as F-band, R1-F3 band, R2-F3 band, plasmon band and M band could be observed on halites based on the color of halites which are due to the defects [19,20]. F centre band formation was due to the anion vacancy with an electron trapped within the crystal structure. The position of the this F band could be observed from the absorption of visible light by excitation of the trapped single electron from ground state to first excited state and it was estimated for NaCl crystal to be around 470 nm. The presence of F centre in the crystal would try to aggregation and form di-F centre, containing two trapped electrons named as F2 or M band which could be observed above 700 nm. Further aggregation would lead to the formation of F3 and F4-centre which are having 3 or 4 negative ion vacancies with equal number of trapped electron within the crystal structure. Over a period of time, the aggregation causes the electrons to associate with isolated alkali ions resulting in the absorption band at shorter wavelength, depending on the particle size. It is also believed that plasmon band would form due to the high density colloidal sodium within NaCl resulting the appearance of blue color. For our samples, we have observed broad absorption band peaks around 400 nm for all samples (Sample C, E, and G but no peak for Sample A) and for sample C, E, and G, peaks around $594.7 \pm 0.2 \text{ nm}$, $585.1 \pm 0.7 \text{ nm}$, $596.6 \pm 0.5 \text{ nm}$ with FWHM as 105, 105 and 110 nm, respectively.

UV absorbance spectra, data shown in Fig. 2., which was due to F band and R2-F3 band. There is some change was observed in the intensity of F band peak (380 to 430 nm), which was due to the variation in the density of F Centers in colored halite crystals. The FWHM and peak area of samples C, E and G were measured as 105, 105, 110 nm, respectively. Population of color Centers were calculated from the FWHM for sample C, E and G as 1.73×10^{18} , 2.10×10^{18} and 2.66×10^{18} , respectively. These samples are natural colored halites and hence The variation in the population

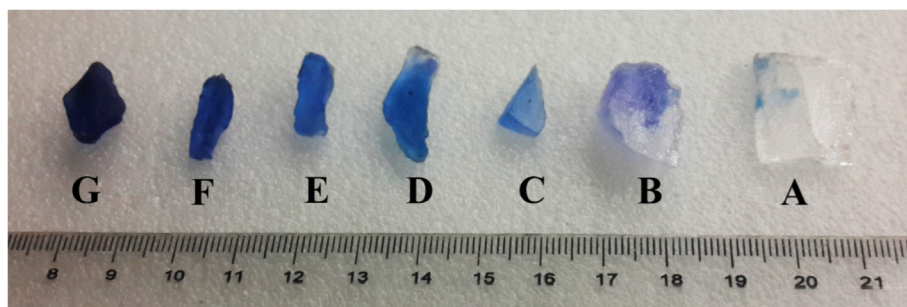


Fig. 1. Photographic image of halite crystals.

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