

**The Color Centers Formation in Chloride Induced by Space Radiation.** Chenan Pan<sup>1</sup>, Wenshuo Mao<sup>1</sup>, Xiaohui Fu<sup>1\*</sup>, Zhongchen Wu<sup>1</sup>, Jiang Zhang<sup>1</sup>, Bo Li<sup>1</sup>, Zongcheng Ling<sup>1</sup>. <sup>1</sup>Shandong Key Laboratory of Optical Astronomy and Solar-Terrestrial Environment, School of Space Science and Physics, Institute of Space Sciences, Shandong University, Weihai, Shandong, China ([foxh@sdu.edu.cn](mailto:foxh@sdu.edu.cn)).

**Introduction:** Chlorides are usually formed by precipitation from evaporating surfaces (e.g., saline lakes) or groundwater/hydrothermal brines, as volcanic sublimates and by efflorescence[1]. The geological environment of saline minerals has high scientific research value because they are potentially geological records of biological activity and chemical sedimentation, which is optimal for the preservation of biological signatures and a high priority for future exploration by orbiting and landed missions.

The halite with ionic lattice is normally featureless. However, when exposing to high-energy charged particles, x-rays and gamma rays in space, halite shows easily recognizable spectral changes in the form of color centers[2]. Because X-rays and energetic particles bombardments can cause crystal structure damage in halite, causing various defects (called color centers) that can trap electrons and form the absorption center of visible light [3]. The halite with color centers may commonly occur on airless asteroids, some planets and planetary satellites. The formation of color centers allows us to identify the original spectral-featureless halite by orbital and in situ spectral survey.

Here, we perform energetic ion/electron and X-ray irradiation experiments on halite. A series of Raman and ASD spectral analysis were used to determine the types color center and investigate their mechanism formation. These spectral results are very important for understanding the presence and formation of color centers in chlorides on celestial bodies. Our results provide clues for the detection of usually uncharacterized chlorides on planets, asteroids and satellites in future missions.

**The formation of color centers:** NaCl crystals can develop color centers in a variety of ways, such as heating the crystals in metallic vapors, introducing impurities, exposure to high-energy radiation, and electrolysis. In a recent study of Ceres, the spectral signature of irradiated halite observed by the researchers suggests one or more possible sources of radiation: (a) solar ultraviolet photons, (b) charged solar wind particles, (c) solar energetic protons, and (d) galactic cosmic rays[4].

The coloration of halite involves a variety of color centers and color center clusters within the ionic NaCl crystals, including the F center, M center, R center, N center, H center,  $V_K$  center and plasmons[5]. The experiments in the present study focused on the

formation of color centers in NaCl under high-energy radiation such as X-rays, beta rays, high-energy ions, etc. In our irradiated samples, F - center, M - center and Na colloids are the most common types. The F center is the simplest defect form, which consists of an electron trapped within an anion vacancy. Two adjacent F-centers in the crystal can aggregate and form a lattice defect containing two trapped electrons, called M center. Further diffusion of F centers leads to the formation of complex F center aggregates ( $n_F$ ) and metal colloids (e.g., Na colloids mentioned above).

**Experiments:**  $H^+$  irradiation was performed using LC-4 high energy ion implanter at the Institute of Semiconductors, Chinese Academy of Sciences. The experiments were carried out at room temperature, in an ion pumped ultra-high vacuum (UHV) chamber with residual pressure of 10-7mbar. The energy of  $H^+$  ions is 30 keV. The irradiation fluence is  $1 \times 10^{15}$  ion/cm<sup>2</sup>.

The main equipment of  $\beta$ -ray radiation is Rhodotron TT200 high energy electron accelerator produced by IBA (Belgium) with a maximum electron energy of 10MeV, a maximum beam current of 8mA and a maximum power of 80kW. The room temperature was 19°C and the room humidity was 22% during the experiment. The radiation dose used in each experiment was 16kgy. The radiation times were 1 to 5.

X-ray irradiation was conducted using the X-ray tube equipped on a Rigaku Ultima IV X-ray diffractometer. The  $CuK\alpha$  X-ray wavelength is 1.5406 Å and the corresponding energy is 8.04 keV.

The reflection spectrum was measured using the ASD FieldSpec4 spectrometer. The ASD spectrometer consists of three detectors that together cover the entire range of 350-2500 nm. The spectral resolution is 3nm in the 350-1000nm region and 10nm in the 1000-1800nm and 1800-2500nm regions.

The Raman spectra of NaCl samples were obtained using a Renishaw inVia Raman system under 532 nm laser excitation. A 50x objective lens with a long working distance was used to focus the laser beam on the sample surface and measure the Raman spectrum. The Raman shift of each spectrum covers the range of 10-1300  $cm^{-1}$ , and the spectral resolution is better than 1  $cm^{-1}$ . The exposure time was 5 seconds.

**Result:** FIG. 1 shows the Raman spectra of X-ray,  $H^+$  implantation, and  $\beta$ -ray radiation. Halite exposed to X-ray has sharp Raman peaks centered at 154 and 172  $cm^{-1}$ , while halite samples irradiated by  $H^+$  ion and  $\beta$ -ray radiation exhibit broad Raman peaks centered at 114

and  $178\text{ cm}^{-1}$ . Although Raman's signature does not determine the types of color center in halite, it shows the presence of Na colloids.

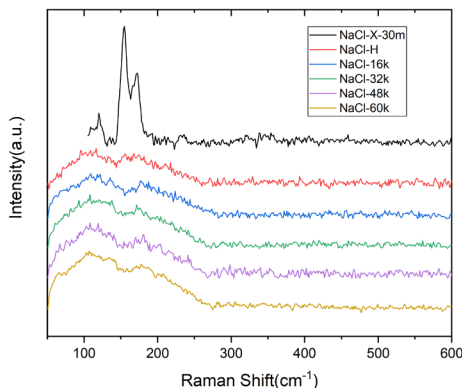


FIG. 1. Raman spectra of halite samples after X-ray, H<sup>+</sup> and β-ray radiation. The Raman data from top to bottom are X-ray, H<sup>+</sup> implantation, and β-ray radiation of 16, 32, 48, and 60keV.

FIG. 2 shows the VIS-NIR reflectance spectra of halite samples collected by ASD spectrometer. It can be noted that strong absorption features exist at 0.464 and 0.725 μm. For sodium chloride, radiation-induced color centers at 0.464 and 0.720 μm correspond to F and M centers[6]. We also noted that for β-ray radiation experiments, the presence and intensity of color centers vary with the radiation dose.

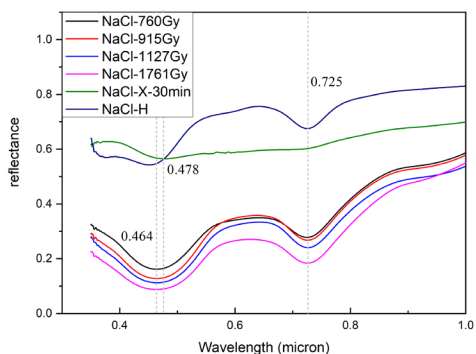


FIG. 2. VIS-NIR reflectance spectra of halite samples after X-ray, H<sup>+</sup> and β-ray radiation.

FIG. 3 shows the continuum removed VIS-NIR reflectance spectra. The band centers and strength of the absorptions due to F and M color centers can be observed more clearly. Furthermore, in FIG. 2 and FIG.3, in the experimental data of H ion implantation, the absorption corresponding to F color center has a certain deviation, which appears at 0.450 μm, which needs further discussion.

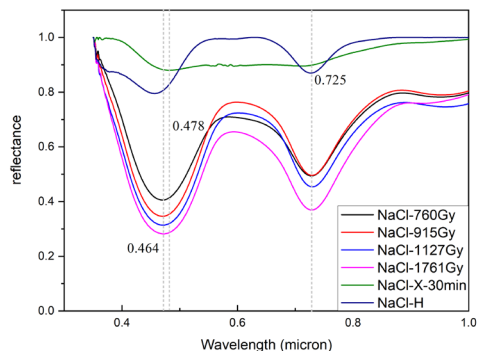


FIG. 3. Continuum-removed VIS-NIR reflectance spectra of halite samples after X-ray, H<sup>+</sup> and β-ray radiation.

#### References:

- [1] M. M. Osterloo, V. E. Hamilton, J. L. Bandfield, T. D. Glotch, A. M. Baldridge, P. R. Christensen, L. L. Tornabene, F. S. Anderson. Chloride-Bearing Materials in the Southern Highlands of Mars[J]. Science, 2008, 319(5870).
- [2] Eastes John W.. Spectral properties of halite-rich mineral mixtures: Implications for middle infrared remote sensing of highly saline environments[J]. Remote Sensing of Environment, 1989, 27(3).
- [3] Frederick Seitz. Color Centers in Alkali Halide Crystals. II[J]. Reviews of Modern Physics, 1954, 26(1).
- [4] Bramble Michael S., Hand Kevin P.. Spectral Evidence for Irradiated Sodium Chloride on the Surface of 1 Ceres[J]. Geophysical Research Letters, 2022, 49(3).
- [5] E. Cruz-Zaragoza, V. Chernov, R. Meléndrez, M. Barboza-Flores. Gamma-radiation effects on NaCl:Cu crystals[J]. physica status solidi (a), 2009, 206(7).
- [6] K. Schwartz, A. E. Volkov, M. V. Sorokin, C. Trautmann, K.-O. Voss, R. Neumann, M. Lang. Effect of electronic energy loss and irradiation temperature on color-center creation in LiF and NaCl crystals irradiated with swift heavy ions[J]. Physical Review B, 2008, 78(2).