



Spectroscopic studies on blue halite

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ABSTRACT

Natural halite displays wide range of colors which is considered as mineralogical rarity. Such variation suggests that the said cubic crystal structure can harbor a great variety of lattice defects as color centers. Raman spectroscopy is the powerful tool for investigation of mineralogical phases as well as very sensitive to the defects formed in crystal structure. Amongst various types of color centers (F, R₁, R₂, M – centers and Plasmons) found in natural colored halite samples, F-centers in present colored halite samples have been confirmed using Photoluminescence (PL) analysis. Detail Spectroscopic studies using Micro-Raman spectroscopy and Photoluminescence (PL) indicate that the blue coloration of the studied halite crystals is due to stoichiometric excess of metallic sodium (Na-colloids) in crystal lattices.

1. Introduction

Deep geological disposal of high level nuclear wastes is currently viewed as the safest route to isolate the toxic waste from ‘man and environment’. The concept is based on ‘multiple barrier system’ which includes ‘natural barrier system’ such as host rock and ‘engineered barrier system’ i.e. waste matrix, canister, overpack and buffer materials from core to the periphery. Geological repositories are constructed within suitable host rocks like basalt, granite (and other crystalline rocks), salt deposits etc and at a depth of 500–1000 m from surface. Key factors which support this methodology include (i) containment of toxic elements within geological repository due to sluggish toxic-element release rates, (ii) long travel times for radionuclides from the waste to the environment due to sorption within buffer materials and host rocks. In this context, the present study on natural halite become important in two aspects, (a) it is one of the dominant constituent of salt deposits – a candidate host rock [1,2] and (b) ionic bonds similar to those present in halite (monovalent cation – halogen anion) exist or are expected to exist within inert matrices proposed for immobilization of next generation of nuclear wastes.

Halite is essentially NaCl compound belonging to cubic crystal system. Ideally it should be colorless transparent in appearance, but in nature it displays wide range in color variations such as milky white, brownish, grayish, or bluish black, smoky, pink, red, lavender, violet, purple, yellow, green, pale or dark blue etc [3]. Colored halite is therefore considered as mineralogical rarity, and the one referred in the present article, belong to the blue variety.

More than two decades back, Sonnenfeld in his excellent review on natural halite narrated few distinguishing properties of blue halite that differentiates it from ordinary rock salt [3]. These include crystallographic features like conchoidal fracture pattern, birefringence and pleochroism, irregular shape and randomly distributed pleochroic halos, physical attributes like higher hardness, lower refractive index and chemical properties including easily dissolution in water, promoting alkaline reactions and higher pH etc. Blue halite therefore has attracted scientists since long but still consensus has not reached on the origin and relationship of its various properties [3–14].

Several theories, based on radioactive and non-radioactive origins, have been put forwarded for hues of natural halite crystals. The factor which is common among all these is the existence of ‘F-Center’ within halite crystal lattice. Originally derived from German terminology ‘Farbzentrum’, ‘F-center’ is a type of crystallographic point defect in where an anionic vacancy is filled by one or more unpaired electrons for charge neutrality (Fig. 1). These electrons absorb photon and emit light in the visible spectrum making a colorless transparent crystal colored. Greater numbers of F-centers make crystals (e.g. alkali halides) more intensely colored.

Formation of F-Centers within alkali halides is believed to be due to interaction between ionizing radiation and halogen ions. Ionizing radiation of appropriate energy can free an electron through knocking it out from outer orbit of halogen anion and thereby converting it into an atom (which can occupy interstitial position). This free electron then moves through the crystal lattice until it gets trapped within a pre-existing anion vacancy. Under this scenario the captured electron is

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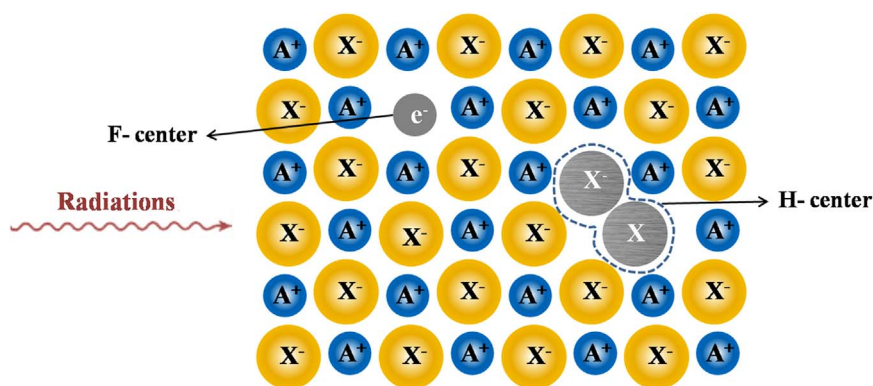
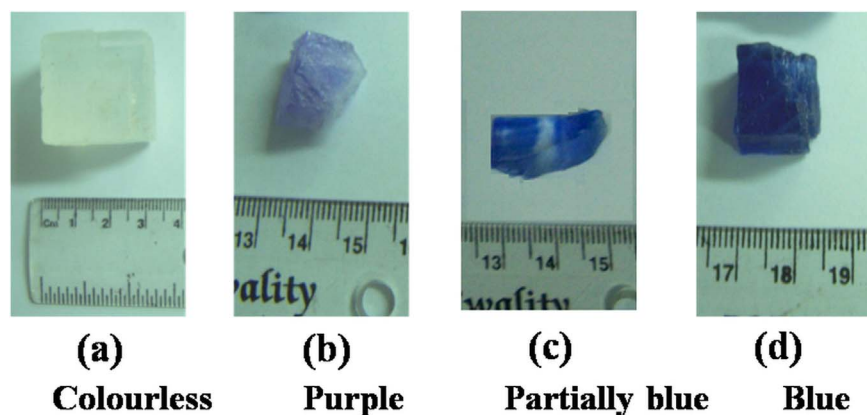
Fig. 1. F- and H-centers in A^+X^- ionic crystal.

Fig. 2. NaCl halite single crystals from salt mine of Morsleben, Saxony-Anhalt, Germany – (a) Colorless; (b) Purple; (c) Partially blue; (d) Blue. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

surrounded by 6 alkali cations, and creates a ‘F-center’. The halogen atom left within the lattice can further interact with another halogen anion to form ‘molecular ion’ such as Cl_2^- , which is commonly referred as ‘H-center’ point defects (Fig. 1). Further, coagulation of such point defects has been described in literature [4] and clusters formed from 2, 3 and 4 F-centers are designated as M, R and N-centers respectively. Such coagulations of sufficient numbers lead to colloid formation commonly referred as sodium sub-chloride (Na_2Cl) or sodium particles. Similarly chlorine atoms cluster to form trapped molecular chlorine. Available data suggests that halite on being exposed to ionizing radiation at high temperature ($\sim 100^\circ C$; which is very much expected within geological repositories over a significant time scale) form metallic sodium and chlorine bubbles [15]. All these defect related features enhanced overall energy content of the host crystals which remain within the system as ‘stored energy’. Nature, distributions, surface structure of these colloids and their responses to ionizing radiation over long time scale (thousands of years) are yet to be understood fully. Earlier investigations using positron annihilation technique showed that colored alkali halides have a characteristic long-lived component, with a mean life $\tau_3 \approx 1-2$ ns, and two photon angular correlation curves narrower than colorless transparent crystals [16]. Strong broad absorption and fluorescence bands have been observed in the near ultraviolet, visible, and near infrared regions in case of alkali halide having F-centers in to their crystals. Information about interaction of these F-centers with lattice vibrations can be obtained from their spectroscopic analysis. UV–vis spectroscopic analyses of blue halite single crystals from Klodawa salt mine, Central Poland, showed dominance of R_2 centers (alongwith plasmons) in navy blue and pale blue crystals, whereas presence of R_1 centers together with maximum Plasmon population was seen in purple variety [17,18]. Raman spectroscopic studies have been extensively used to find out defects and type of inclusions present in rock salts and halite minerals [19–22]. However, Raman spectra of color centers in alkali halides differ from sample to sample of same composition as it primarily depends on

conditions of formation of defects and occurrence of colloids. In this work, micro-Raman spectroscopic investigation of colorless and colored halite samples gives better insight of formation of colloids along with defects.

Also, considering the existence of wide range of point defects, it is therefore felt interesting to characterize blue halite with some additional spectroscopic like Photoluminescence. Photoluminescence is the light emission of from matter after the absorption of electromagnetic radiation. Photoluminescence spectroscopy can be used for identification of ionic impurities present in colored minerals. It also helps to understand valance state of particular ion and its coordination [23]. Three types of measurements i.e. absorption, emission and excitation spectroscopy comes under the category of luminescence spectroscopy [23]. In this work, we are exploring emission, excitation and life time spectroscopic analysis to understand the luminescence mechanism in blue halite.

2. Experimental

Different halite single crystals with color variation are collected from salt mine of Morsleben, Saxony-Anhalt, Germany. Different single crystals collected from this area are shown in Fig. 2 and classified as transparent colorless, purple, partially blue and blue varieties. In field outcrops as well as in hand specimen scales, color variation was found to be dependent on crystal size. Usually larger single crystals (2 cm and above) are found to be euhedral in nature with ink blue/navy blue color patches, having random orientations with respect to cleavage planes. Smaller sized crystals which dominantly exhibited blue/light blue/purple color patches were of either anhedral or subhedral shapes. Colorless transparent variety existed in all grain size and shape ranges. For the present study, single crystals samples were prepared using cleavage properties of halite. To avoid any influence of external contamination on spectroscopic data, original cleaved surfaces were actually measured; therefore no sample preparations using grinding and

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