IRRADIATED SALTS AND THE COLOR OF THE NONICE MATERIAL ON EUROPA

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Introduction: The composition of the nonice material on the surface of Europa is a mystery remaining to be unraveled. Europa is deep within the Jovian radiation belts and energetic charged particles continuously bombard its surface. This weathering destroys bonds in the crystals, amorphizing the water ice on its surface [1], altering the structure of the nonice material, and modifying the surface composition through the deposition of Iogenic oxygen and sulfur that can form S-O bonds [2] and more complex sulfur-bearing molecules [3]. Infrared spectral analyses indicate that this nonice material is likely a salt of Mg, Ca, and/or Na or sulfuric acid [e.g. 3-9] with chemically bound waters of hydration. The current best spectral match in the infrared is possibly being a combination of frozen magnesium sulfate brine and hydrated sulfuric acid [e.g. 7,9]. However, the efficacy of spectral matching in the infrared with NIMS is limited by relatively coarse spectral resolution (26 nm) and similarly coarse spectral sampling, for which diagnostic spectral features of specific mineralogy could be missed [e.g. 9]. In our work, we follow upon previous research into the formation of color centers in salts [10] to explore the possible role of radiation-induced dislocation defects that are optically active to explain the visible spectrum of the nonice rich terrain on Europa and to provide more information on the composition of the hydrated nonice material .

Color centers are optically active dislocation defects induced by high energy particulate (100s of eV to MeV) electron and proton irradiation of primarily salts such as alkaline halides (NaCl, KCl), and earth-alkaline halides such as CaF_2, MgF_2, $MgCl_2$, and $CaCl_2$ but also in other salts. The defects are generally formed through the production of Schottky pairs (cations and anions ejected into the crystal lattice), leaving a hole pair, with the anion vacancy being replaced by an electron that is subsequently held in position by the remaining surrounding cations.

We extend the work of Hand and Carlson work investigating the spectral characteristics of color centers, expanding our investigations to a suite of sulfates, carbonates, and halides. Samples were irradiated with 40keV electrons at a fluence of ~80 microamps to a dosage equivalent of about 10E5 yrs of weathering on the trailing hemisphere of Europa. Spectra are obtained from ~ 200 nm to at least 2400 nm at a resolution of 2 nm in the near ultraviolet and 10 nm in the visible and near infrared. We show spectra only out to 1300 nm because there were no unique spectral changes at longer wavelengths other than due to sample desiccation. Near UV spectra were obtained immediately after the irradiation was completed while the sample remained in vacuum. The Vis-NIR spectra were obtained in a nitrogen purged environment

Results & Discussion: This electron radiation affected the reflectance and spectral characteristics of all salt samples in the near ultraviolet and visible wavelengths. All irradiated samples were darkened in the NUV – Visible, and for some salts the darkening extended into the SWIR. Most salts also developed individual absorption features at visible wavelengths that to some extent correlate within classes of salts (halide, carbonate, sulfate). When pristine before irradiation, these salts are uniformly bright in the visible through the NIR, except for the $FeSO_4$, which has a strong crystal field absorption near 1 micron due to the presence of the Fe^{2+} ion. The reflectance of each decreases in the NUV shortward of 300 nm due to oxygen-metal charge transfer; the OMCT band due to Fe^{2+} is exceptionally strong and is responsible for its lower reflectance into the visible,.

Halides: Upon irradiation the two halides investigated, NaCl and KCl, develop multiple bands in the visible and near infrared. NaCl darkens dramatically shortward of 1000 nm, with the color center bands located at 450, 575, and 725 nm. Hand and Carlson (2015) noted similar bands centered at 460 and 723 nm, but did not observe a band near 575 nm. KCl darkens more uniformly with wavelength with individual absorption features at 550 nm, 735 nm, and 827 nm, but not in the near UV.

Sulfates: We examined $MgSO_4$, $FeSO_4$, and Na_2SO_4. The doubly-charged cationic sulfates behave similarly to each other, and differently from the Na_2SO_4 and from the halides. After irradiation, the Mg and Ca sulfates brown in the visible but do not change in the NIR, nor do discrete color centers form. In contrast, the entire visible – SWIR spectral region of the Na_2SO_4 darkens by about 20%. Additionally, a strong color center forms that is centered at 610 nm.

Carbonates. Similar to the behavior of the sodium sulfate, the singly-charged cationic carbonate, Na_2CO_3 darkens significantly in the visible through the near IR and develops a single strong absorption feature, centered at 580 nm imbuing a purple color to the pellet. The $CaCO_3$ browns and develops a strong band at 600nm, but is not affected in the near IR.

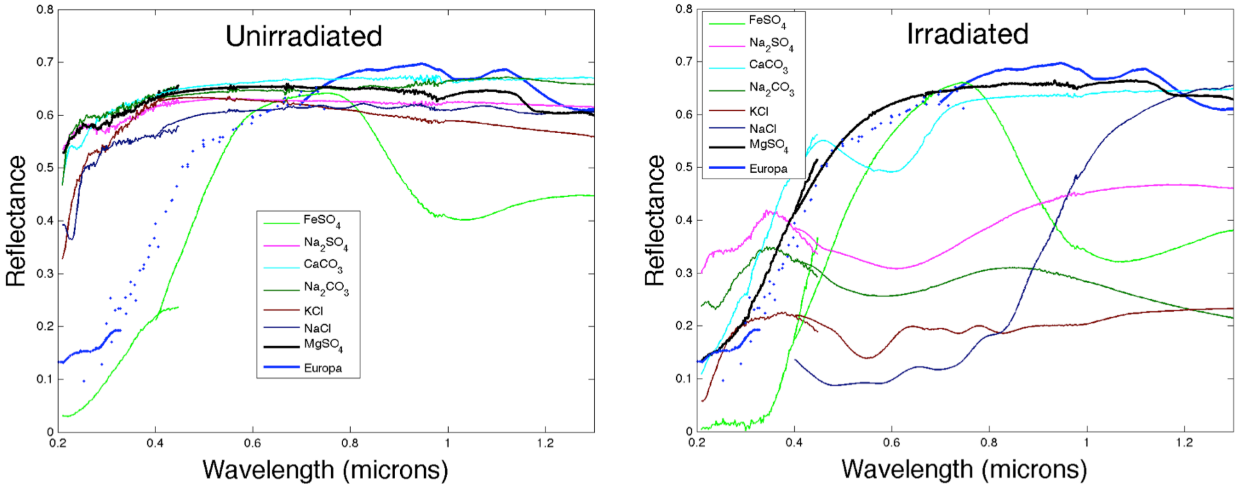

Figure 1. The NUV to NIR spectra of salts (scaled) compared to the telescopic spectrum of the trailing hemisphere of Europa from digitized from [11]. Pristine salts are all featureless but all salts are affected by the electron bombardment. Only $MgSO_4$ changes to become spectrally consistent with the spectrum of Europa. Most other salts have discrete color center absorption features that are inconsistent with Europa, or darken and redden at wavelengths longer than seen for the trailing side of Europa.

Results are consistent with previous research, showing that energetic electron bombardment forms color centers in halides. We have found that carbonates and sulfates also form color centers. Carbonates and sulfates of singly charged cations darkened throughout the visible and into the infrared, whereas those minerals with doubly charged cations did not. Halides darkened into the near infrared and also formed multiple weak color centers compared to just one or a few strong color centers in sulfates and carbonates. Additionally, the color centers in all salts are stable over laboratory timescales at room temperature, although for some samples, color centers did begin to fade and samples brighten over days, and if warmed by only a few 10s of degrees, fading could occur immediately. The wavelength positions of the absorption features associated with color centers vary with composition and if these features are detected on a body, could be diagnostic of specific salt composition.

Of all the salts irradiated in this work, $MgSO_4$ and $FeSO_4$ only browned and formed no discrete absorption features (Figure 1). Furthermore, because the $MgSO_4$ salt possess no other absorption features, the NUV through NIR spectrum of irradiated $MgSO_4$ appears most consistent with that of the nonice dark material on the trailing hemisphere of Europa. The spectra of the halides and carbonates on the other hand are not consistent with the spectrum of Europa, all having absorption features that are not detected in telescopic observations..

Conclusions: Salts exposed on Europa's surface will quickly weather to form color centers. These spectral features, being uniquely dependent on composition, can potentially enable compositional identification of these materials not only on Europa, but also on any surface embedded in a strong radiation environment. The near-UV to visible spectrum of the nonice, dark material on Europa's trailing hemisphere is best matched by the spectrum of post-irradiated $MgSO_4$ and is not matched by the spectra of the other salts that were irradiated.

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