"Glow-in-the-dark" materials, familiar to most travelers via airplanes or cruise ships, are frequently utilized for self-lit emergency exit signs, featuring a green afterglow known as persistent luminescence (PeL).

Divalent europium doped synthetic strontium aluminate, commonly referred to as hackmanite, presents an intriguing avenue for exploration, as its afterglow remains largely unexamined. Despite this, synthetic versions show promise in rivalling some of the leading commercially available persistent luminescence (PeL) materials. The findings from these investigations not only illuminate the PeL phenomenon but also offer valuable insights for enhancing the performance of synthetic materials.

Hackmanite, a mineral typically found in nepheline syenites, phonolites, and similar rock formations, as well as in metasomatized calcareous rocks and cavities of volcanic blocks, is renowned for its distinctive property of displaying purple tenebrescence. This phenomenon, characterized by reversible photochromism, occurs upon exposure to UV and X-rays.

Investigate the factors influencing the manifestation of persistent luminescence in natural hackmanites, presenting a quantitative analysis of their PeL and optical energy storage characteristics. This study examines five natural hackmanite samples sourced from different locations: Greenland, Mont Saint Hilaire (Canada), Koksha Valley (Afghanistan) - represented by two separate samples, and Pakistan. The research explores the relationships between the composition, concentration of various impurities, and the observed PeL phenomenon.

MATERIALS AND METHODS Natural hackmanite samples were acquired from private collectors. The crystal structure was determined using X-ray powder diffraction measurements. Elemental composition analysis was conducted using a Bruker Tornado M4 micro-XRF spectrometer or a PANalytical Epsilon1 device. Photoluminescence characteristics were examined using UV lamps, specifically UVP UVLS-24 with 4W at 254/365 nm or UVP UVM-57 with 6W at 302 nm. Persistent luminescence was measured using a Hagner ERP-105 luminance photometer. Photon counting experiments were performed to assess storage capacity. Elemental distributions were determined through SEM-EDX point analyses. Statistical analysis was conducted using IBM SPSS Statistics 24.0 software.

METHODS

Energy levels were determined by combining density functional theory (DFT) periodic boundary condition calculations. Geometry optimizations were performed using the CRYSTAL17 code with the global hybrid functional PBE0. Mössbauer spectra were obtained with a Doppler velocity of approximately 2.0 mm/s and calibrated using α-Fe. A nonlinear least-squares fitting program was utilized to determine the quadrupole coupling constant, relative component intensities, and the isomer shift δ relative to α-Fe.

Figure 2 depicts photoluminescence spectra under continuous LED excitation at varying wavelengths (a) 355 nm, (b) 295 nm, and (c) 255 nm, along with cathodoluminescence spectra (d).

(a) Excitation at 355 nm: All samples exhibit the characteristic orange emission of S2− entities.

(b) Excitation at 295 nm: Most samples display a blue/green emission peaking at approximately 500 nm.

(c) Excitation at 255 nm: With this wavelength, all samples except Greenland and Mt. St. Hilaire exhibit the blue/green emission band.

For Greenland samples, the emission is attributed to disulfide, while for Mt. St. Hilaire samples, a peak at 720 nm is observed.

(d) Cathodoluminescence spectra: This combines all signals, showcasing a strong UV/blue band peaking at 350 nm for natural samples and at 364 nm for the synthetic sample.

In Figure 6a, an electron's excitation from Ti3+ to the conduction band occurs at approximately 3.7 eV (335 nm), consistent with the PeL excitation threshold energy.

Figure 6b presents Mössbauer measurements for the Mt. St. Hilaire sample, which exhibits the highest Fe content and shortest PeL duration.

Figure 6c showcases the photoluminescence excitation spectrum of Fe3+ in hackmanite.

In Figure 6d, it's demonstrated that the tenebrescence process efficiently decreases PeL. Additionally, the presence of sulfur correlates with a weakening of PeL. Furthermore, the incorporation of potassium into the structure results in a reduction in overlap as the potassium concentration increases.