

Identification of Eu Oxidation States in a Doped Phosphor by TOF-SIMS Imaging

Overview: Luminescent compounds and materials have numerous uses, most notably in detectors of various sorts but also in consumer products such as displays, LED lighting and watches. The device, or application, in which a luminescent material is used depends largely on its emission properties including color, brightness and decay rate. The emission properties, whether of a fast decay rate fluorescent material or a slow decay rate phosphorescent material, are defined by the chemical composition and the physical structure of the luminescent material. The brightness and the decay rate can be affected significantly by trace contaminants, or poisons. In this Note we use the PHI *nanoTOF* to visualize the trace-level chemical inhomogeneities in a Eu-doped phosphor powder, $\text{Sr}_5(\text{PO}_4)_3\text{F}:\text{Eu}$. The Eu dopant is present in the +3 oxidation state, Eu(III), throughout the phosphor; however, the phosphor is thought to be poisoned with trace quantities of the +2 oxidation state, Eu(II). A characteristic of time-of-flight secondary ion mass spectrometry (TOF-SIMS) is the ability to visualize chemical information in a spatially resolved manner. TOF-SIMS also combines parallel detection so that the entire mass spectrum is available for chemical identification with high sensitivity so that trace-level chemistries may be identified. The PHI *nanoTOF* is uniquely equipped for chemical imaging of topographically rough surfaces, a distinguishing characteristic that is necessary for this chemical imaging application.

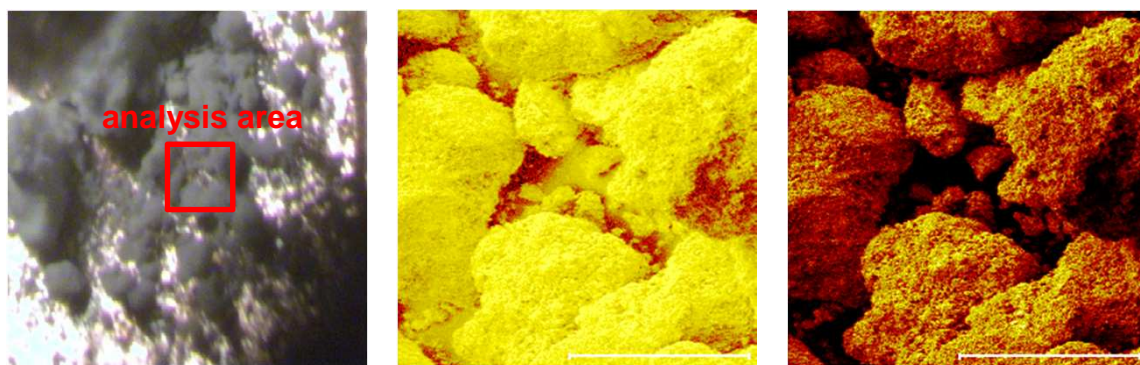


Figure 1. Images of the Eu-doped phosphor powder. (LEFT) Optical image (approx. 1.2 mm x 1.2 mm) at the analysis position. The powder particles range in size from ~ 20 μm to ~ 100 μm . The approximate analysis area is identified. (CENTER) Total ion image (+SIMS) of the phosphor particles within a 200 μm x 200 μm field-of-view (the marker is 100 μm) showing all surfaces of the particles as well as the underlying adhesive tape. (RIGHT) Ion image of Sr^+ (88 m/z), a matrix constituent of the phosphor powder, revealing only the phosphor particles in the 200 μm x 200 μm field-of-view (the marker is 100 μm).

Experimental: The phosphor powder was used in the as-received state and mounted onto a silicon substrate using double-sided hydrocarbon tape. All TOF-SIMS measurements were made on a PHI TRIFT V *nanoTOF*. A 30 keV Au^+ primary ion beam, operating at a DC current of 100 pA, was used to acquire chemical images of the phosphor in both the positive and the negative secondary ion polarities. The analytical field-of-view was 200 μm x 200 μm with a 256 pixel x 256 pixel digital raster, and the primary ion dose was maintained well within the static limit, i.e. $\leq 1.2 \times 10^{11}$ Au^+/cm^2 , for each analysis. Charge compensation was easily achieved with ≤ 15 eV e^- and ≤ 10 eV Ar^+ of the PHI-patented dual-beam charge neutralization system. A raw data stream file was collected to allow full post-acquisition evaluation (i.e. retrospective analysis) of the data.

Results: An optical image of the phosphor powder, and a corresponding TOF-SIMS total ion image of a 200 μm x 200 μm field-of-view, are shown in Figure 1. These images reveal the severe topography of the powder which has particles ranging in size from approximately 20 μm to approximately 100 μm . Nevertheless, the spectrometer of the *nanoTOF* allows efficient and uniform collection of secondary ion signals from all parts of the particles for full chemical characterization.

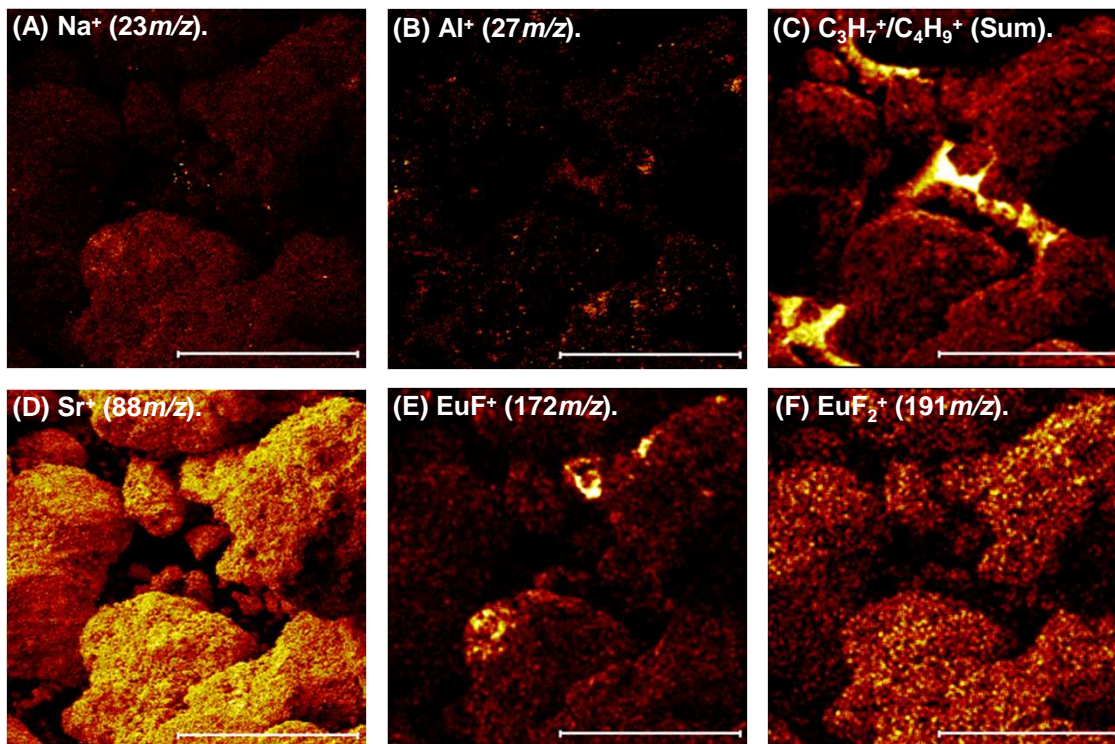


Figure 2. TOF-SIMS chemical images of the Eu-doped phosphor powder. Each image was collected in the positive secondary ion polarity (+SIMS) and shows specific elemental or chemical distributions across the surface of the particles observed within a 200 μm x 200 μm field-of-view (the marker is 100 μm). The organic fragments shown in panel (C) arise from the mounting tape and are observed to have contaminated the powder surface during mounting.

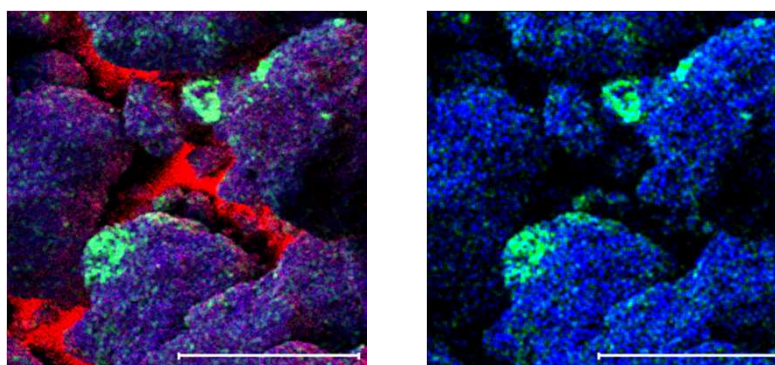


Figure 3. (LEFT) False-color overlay of the $\text{C}_3\text{H}_7^+/\text{C}_4\text{H}_9^+$ organic fragments (image sum; red), the Eu(II)F^+ poison (172 m/z ; green), and the Eu(III)F_2^+ dopant (191 m/z ; blue). (RIGHT) False-color overlay of the Eu(II)F^+ poison (172 m/z ; green) and the Eu(III)F_2^+ dopant (191 m/z ; blue). The field-of-view is 200 μm x 200 μm , and the marker is 100 μm . Note that while the Eu(II) poison is distributed throughout the phosphor particles, the localization observed within certain particles improves the confidence regarding the identification of a distinct Eu oxidation state in the absence of pure reference materials.

Several elemental and chemical images of the phosphor particles are revealed in Figure 2. The hydrocarbon mounting tape is observed in Figure 2(C). Some hydrocarbon signal is observed across the surface of the phosphor particles which ostensibly arises from contamination produced during the process of sample mounting. The phosphor is strontium-based as the image in Figure 2(D) illustrates, wherein each particle is clearly observed. The phosphor is doped with Eu in the +3 oxidation state, Eu(III) , which is clearly observed as EuF_2^+ in Figure 2(F) to be homogeneously distributed throughout the particles as a fluorine complex. Note that fluorine is a known constituent of the phosphor composition. Figures 2(A) and 2(B) reveal an inhomogeneous distribution of Na^+ and Al^+ contamination.

Based on the emission characteristics of the phosphor, it was suspected that some of the Eu dopant had been reduced to the +2 oxidation state, Eu(II). The image of EuF^+ in Figure 2(E) reveals a distribution of Eu(II) that is highly inhomogeneous and distinct from that of the Eu(III) dopant. The differences in spatial distribution of EuF^+ and EuF_2^+ indicates that the appearance of these species is not related to simple ion fragmentation (i.e. a “SIMS effect”), nor can it be explained by a difference in fluorine distribution. Rather, it is likely that these components arise from a difference in the oxidation state of Eu.

Conclusion: TOF-SIMS chemical imaging was conducted on a Eu-doped phosphor with the PHI TRIFT V *nanoTOF* to observe the differences in oxidation state and distribution of the Eu dopant and poison. The high sensitivity of TOF-SIMS enables detection of species having a low abundance, and the parallel detection capability allows full molecular and isotopic characterization of the matrix chemistry. A particular strength of the PHI *nanoTOF* as it relates to the analysis of the phosphor particles is the TRIFT mass spectrometer which is designed for efficient and uniform collection of secondary ions from all parts of topographically rough samples. This inherent quality of the PHI *nanoTOF* provides chemical visualization without image artifacts, a specific advantage for measurements of particles such as a phosphor powder.

Acknowledgements and References:

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