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$EuKNaTaO_5$: Crystal Growth, Structure and Photoluminescence Property

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The need for new optical materials for use in flat panel displays, optoelectronic devices, and biomedical imaging and sensing applications continues to advance the field of lanthanide doped luminescent materials, where the development of new materials that emit in the visible portion of the electromagnetic spectrum when excited by higher energy visible light is of particular interest.[1] Many of the trivalent lanthanides display luminescence due to the ease with which excited states can be populated, coupled with the prevalence of radiative rather than nonradiative decays to the ground state. Trivalent europium specifically has attracted attention due to its intense luminescence around 610 nm that can be generated by visible light excitation.[2] The local environment plays a crucial role in the intensity of this luminescence, and hence, many inorganic materials, including oxides,[3,4] nitrides,[5] and other matrices,[2] have been evaluated as hosts for luminescent lanthanides. In such doped systems, typically, the luminescence reaches a maximum at a low doping level, around 2−3%, and subsequently decreases with increasing lanthanide doping concentration due to concentration quenching.[1−4,6−8] For this reason, the observation of intense luminescence at 608 nm upon excitation at 535 nm in the novel bulk europium containing tantalate $EuKNaTaO_5$ was unexpected. (Figure 1A).

Complex niobates and tantalates comprise a large group of metal oxides that exhibit a variety of intriguing optical properties[7−11] including intrinsic photoluminescence.[9,11] Many niobates and tantalates function as a photoactive host materials when doped with optically active elements, such as trivalent lanthanides.[8,10] However, since doping has its own problems that can be detrimental to the photoluminescence intensity, including concentration quenching, lattice mismatch, and charge segregation effects,[12] materials that intrinsically exhibit photoluminescence, such as our title compound, have become of interest.

Herein we report the synthesis, structural investigation, and intense intrinsic luminescence of a new tantalate, $EuKNaTaO_5$. This new oxide was obtained during exploratory crystal growth studies in the alkali metal−tantalum−lanthanide−oxygen phase space utilizing molten hydroxides, a method we have used successfully to synthesize other complex oxides with new structure types.[9,13]

Single crystals of $EuKNaTaO_5$ were grown out of a KOH/NaOH eutectic melt contained in either open or sealed silver reaction vessels. (For information on powder synthesis by solid-state reactions, see details in the Supporting Information.)

The crystal structure of the title compound was determined by single crystal X-ray diffraction. The structure, which crystallizes in the tetragonal space group $P4/nmm$, $a = 5.6878(2)$ Å, $c = 8.2258(2)$ Å, consists of sheets of edge-sharing EuO_8 cubes that form a checkerboard pattern. Groups of four edge-sharing cubes of EuO_8 are further edge-shared to the four basal edges of TaO_5 and NaO_5 square pyramids located above and below a vacant cube on opposite sides of the sheet, where the TaO_5 and NaO_5 square pyramids are arranged in alternating rows. The potassium ions occupy the space between the $NaEuTaO_5$ sheets. Figure 1A shows the graphical representation of the $EuKNaTaO_5$ structure. This structure type was first reported by Liao et al.,[14] and other compounds with related structure-types are known.[15]

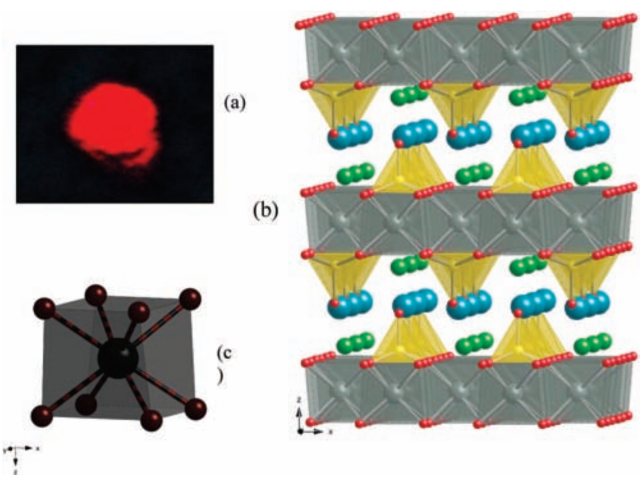

Figure 1. (A) An optical image of the intense room temperature photoluminescence in $EuKNaTaO_5$. (B) Schematic of the crystal structure of $EuKNaTaO_5$ viewed along the *a*-axis. EuO_8 distorted cubes are shown in gray; TaO_5 square pyramids are shown in yellow. K^+, Na^+, and O^{2-} are shown in green, blue, and red, respectively. (C) Local coordination environment of the Eu^{3+} ion.

In this structure, all eight Eu−O distances within the cubes are identical (2.4476(14) Å), which is unusual for Eu^{3+} containing oxides where distorted cubes with more than one bond length predominate. Figure 1C illustrates the local coordination environment around each Eu^{3+} atom. The EuO_8 cubes with eight equal Eu−O bond distances are nonetheless heavily distorted, with O−Eu−O bond angles near 70° and 110°. The distance between europium ions in adjacent cubes is 4.0219(2) Å.

The diffuse reflectance spectra for $EuKNaTaO_5$ (crushed crystals) and Eu_2O_3 are shown in Figure 2A. A commercial Eu_2O_3 powder was taken as a reference. The absorption edges for $EuKNaTaO_5$ and Eu_2O_3 are located around 285 (4.4 eV) and 270 nm (4.6 eV), respectively. The room temperature excitation spectra of both Eu_2O_3 and the title compound are shown in Figure 2B. The strong broadband near 280 nm in the spectrum of Eu_2O_3 is due to charge transfer from O^{2-} to Eu^{3+}; in $EuKNaTaO_5$, by contrast, only a weak charge-transfer band near 300 nm is observed. These broad bands can be attributed to the overall combination of charge transfer transitions in metal−oxygen polyhedra and have been observed and characterized in other oxides.[4] In Figure 2A, two main diffuse reflection peaks attributed to $^5D_2$ and $^5D_1$ transitions from $^7F_{0,1}$ to

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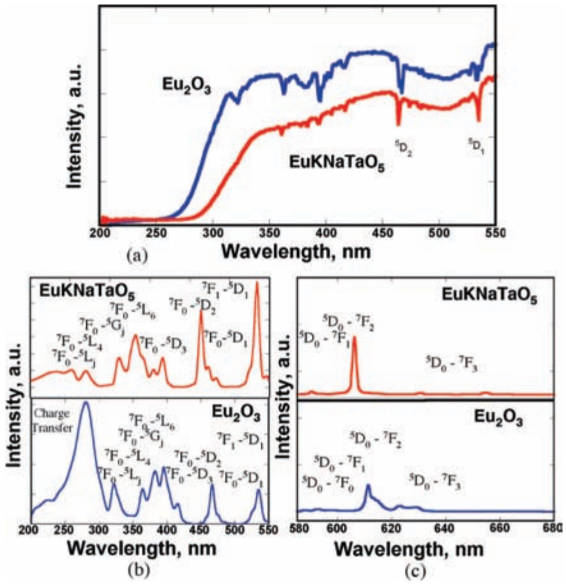

Figure 2. (A) UV−vis diffuse reflectance spectra for Eu_2O_3 and EuKNaTaO$_5$. (B) Excitation spectra for EuKNaTaO$_5$ and Eu_2O_3 for an emission at 608 nm. (C) Emission spectra for EuKNaTaO$_5$ and Eu_2O_3 excited at 535 nm. Data collected on crushed crystals.

excited states of Eu^{3+} can be observed between 450 to 550 nm. These emission lines correspond to the $^7F_0$−$^5D_2$ and $^7F_1$−$^5D_1$ excitation transitions clearly seen in the emission spectrum shown in Figure 2B. In addition to the charge-transfer band, the most intense transition for Eu_2O_3 is around 394 nm, which is a commonly utilized excitation wavelength for the materials used in LED lights. This transition corresponds to the near-UV part of the spectrum; however, it is desirable to be able to utilize the visible region to maximize efficiency. The excitation spectrum of EuKNaTaO$_5$ has the strongest sharp peak at 535 nm, well within the visible (green) part of the electromagnetic spectrum. This is desirable when considering the use of this material in LEDs.

Figure 2C shows the emission spectra of EuKNaTaO$_5$ and, for comparison, that of Eu_2O_3. When excited at 535 nm, the title compound emits at 608 nm, with greater intensity than Eu_2O_3, which emits around 612 nm. Both of these peaks are attributed to the $^5D_0 \rightarrow {}^7F_2$ transition. This transition is sensitive to the coordination environment of the Eu, and the intensity is strongly influenced by the crystal field environment of the rare earth.[2] For EuKNaTaO$_5$, the peak centered at 608 nm is the most intense, which is explained by the crystallographic environment of the Eu atom. The rare earth atom is located on a site with point symmetry D_{2d} (Wyckoff site 2b). Because all eight Eu−O distances are the same, a single peak in the red region (608 nm) is observed, which is due to the electric dipole transition $^5D_0 \rightarrow {}^7F_2$.[16] However, although the Eu−O bond distances are all the same, the heavy distortion of the cube lowers the local point symmetry causing intensification of the peak at 608 nm and loss of intensity of the emission lines generated by other transitions ($^5D_0 \rightarrow {}^7F_J$ ($J = 1, 3, 4$)).[6] The most intense emission line in the spectrum is responsible for the bright orange-red luminescence and can be readily seen. Even though relatively high intensity can be achieved when exciting the Eu^{3+} doped materials at the near-UV region, it is highly desirable to find materials responsive to the visible part of the spectrum. An optical image of the intrinsic bright orange/red photoluminescence in EuKNaTaO$_5$ is shown in Figure 1A. Clearly, the ability to excite EuKNaTaO$_5$ with light in the visible part of the spectrum (535 nm) to generate an intense orange/red emission (608 nm) makes this a very promising material for white light LED applications.

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Supporting Information Available: Synthetic details and crystallographic data of EuKNaTaO$_5$. This material is available free of charge via the Internet at http://pubs.acs.org.

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