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# Seeking the optimal $LaTaO_4$:Eu phosphor

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ABSTRACT

Lanthanum orthotantalate, $LaTaO_4$, is an excellent host lattice for rare-earth luminescent ions such as $Eu^{3+}$ for red emission. However, there are multiple *RE*$TaO_4$ (*RE*=rare earth) polymorphs, and the stability of these is controlled predominantly by the RE-radius. Thus it is difficult to obtain a pure phase of $LaTaO_4$:Eu as Eu concentration and consequently the *RE* radius is varied. We recently reported a 'soft-chemical' route that allows crystallization of pure-phase $LaTaO_4$:Eu at temperatures as low as 800 °C. In the current report, we investigate polymorph evolution and Eu emission as a function of Eu concentration and annealing temperature. We obtain a maximum quantum yield (QY) of 83% at the highest Eu substitution (25%) for which the low temperature orthorhombic (*Pbca*) polymorph is stable. Therefore, QY is not limited necessarily by concentration quenching; rather it is limited by polymorph stability as the RE-radius decreases with increasing Eu substitution.

## 1. Introduction

Europium phosphors are exceedingly important in a variety of technologies including authenticity tagging, fluorescent lamps, and the emerging LED-based solid-state lighting [1]. It is well-known that the Euro banknote (official currency of the European Union) emits red under a UV-lamp, due to the presence of a proprietary europium compound as an anti-counterfeiting measure. Fluorescent lamps contain alkaline-earth aluminates or phosphates doped with $Eu^{2+}$ for blue emission (i.e. BAM:Eu; barium magnesium aluminate) and red-emitting $Eu^{3+}$-doped yttrium oxide. Yttrium oxysulfide doped with $Eu^{3+}$ emits red and is used in CRT displays. Finally, a recently discovered class of phosphors, the alkaline earth nitridosilicates doped with $Eu^{2+}$ [2–6] emit yellow–green or orange–red when excited by a blue LED, and has been found that it can be used in improving color rendering for solid-state lighting (SSL) devices. Every application has a demanding list of requirements for the phosphor material including excitation and emission at wavelengths that are optimal for a given device, high quantum yield (QY), good luminous efficacy of radiation (LER) and minimal thermal quenching.

We and others have recently focused on the development of tantalate and niobate materials as host lattices for $Eu^{3+}$ emission [7–11]. Soft-chemical methods are of particular interest, in that niobates and tantalates are incredibly refractory, generally requiring heating temperatures of 1600 °C to obtain full crystallinity. Both hydrothermal [7,8] and flux [9] syntheses are good approaches; our focus has been largely hydrothermal. In general, our rare-earth tantalate materials feature sharp $Eu^{3+}$ emission at 610 nm when excited with blue light ($\lambda \sim 465$ nm); and they have low thermal quenching, due to the very stable and robust nature of tantalate lattices [7,8]. We have found that large concentrations of $Eu^{3+}$ can be incorporated into these host lattices without decrease in QY due to concentration quenching. In this regard, they are similar to luminescent rare-earth molybdates [12–14], tungstates [15,16], and niobates and tantalates[17,18] in which Eu is a stoichiometric component rather than a dopant. It is generally understood that structural features such as long Eu–Eu distances or lattice bond angles that result in difficulty in energy transfer are responsible for minimal concentration quenching [19,20].

We reported prior a new low-temperature orthorhombic polymorph of $LaTaO_4$ that can be obtained only by soft-chemical synthesis. The low-temperature polymorph does not form directly in the hydrothermal reaction: rather $La_2Ta_2O_7(OH)_2$ forms hydrothermally [21], and is converted into $LaTaO_4$ by heating to 850 °C [7]. Upon further heating to 1100 °C and higher, the low temperature polymorph converts completely into a high temperature polymorph [7]. When the hydrothermal synthesis is carried out with substitution of Eu on the La-site, $La_2Ta_2O_7(OH)_2$:Eu is formed and likewise converted into $LaTaO_4$:Eu, where the low-temperature, orthorhombic polymorph exhibits higher QY of the Eu emission than the higher temperature monoclinic polymorph [7].

In this work, we further explore the synthesis and luminescence characteristics of $LaTaO_4$:Eu polymorphs. In addition to investigating the phases with higher Eu concentration, we also compare the hydrothermal synthesis to traditional solid-state processing. QY, morphology and structural changes of $LaTaO_4$:Eu polymorphs are

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documented as a function of Eu concentration. There are several polymorphs of *RE*TaO$_4$ (*RE*=rare earth) and their stability is strongly dependent on the RE radius (changes linearly with La:Eu ratio). This was also noted prior to comparing the formation of LaTaO$_4$, PrTaO$_4$ and NdTaO$_4$ polymorph as from their respective La$_2$Ta$_2$O$_7$(OH)$_2$, Pr$_2$Ta$_2$O$_7$(OH)$_2$ and Nd$_2$Ta$_2$O$_7$(OH)$_2$ precursors [22]. Thus in the LaTaO$_4$:Eu system, QY optimization is not necessarily limited by concentration quenching, but more likely the interrelated effects of rare-earth radius as a function of Eu concentration and polymorph stability. The coincidence of several polymorphs for some Eu concentrations and annealing temperatures quickly renders QY optimization difficult to understand and control. However, we have empirically determined optimal Eu concentration to be ~25%: the maximum concentration at which the low temperature polymorph dominated, and an impressive QY of 83% was obtained.

## 2. Materials and methods

### 2.1. Synthesis

#### 2.1.1. LaTaO$_4$:Eu via 'soft chemistry'

LaTaO$_4$:Eu via the hydrothermal route was synthesized using methods, which we have previously reported [7,21]. La$_2$Ta$_2$O$_7$(OH)$_2$:Eu is synthesized hydrothermally. Lanthanum nitrate La(NO$_3$)$_3\cdot$6H$_2$O (Aldrich, *FW*=433.02) (0.411 g for 5% Eu-doped, 0.389 g for 10% Eu-doped, 0.346 g for 20%, 0.325 g for 25%, 0.303 g for 30%, 0.281 g for 35%, and 0.259 g for 40%) and europium nitrate, Eu(NO$_3$)$_3\cdot$5H$_2$O (Aldrich, *FW*=428.05) (0.021 g for 5% Eu-doped, 0.043 g for 10% Eu-doped, 0.086 g for 20%, 0.107 g for 25%, 0.128 g for 30%, 0.150 g for 35%, and 0.171 g for 40%) are combined in proportional amounts and dissolved in 12.5 mL of DI (deionized) H$_2$O. The total amount of lanthanum and europium salt is 1.0 mmol. Potassium citrate (0.357 g, 1.0 mmol) is dissolved separately, also in 12.5 mL of DI H$_2$O and added drop-wise into the dissolved lanthanide salt solution while stirring vigorously. Addition of the potassium citrate produces a thick white precipitate, which then redissolves after thirty drops of 4 M aqueous KOH solution is added. The potassium peroxotantalate salt K$_3$[TaO$_2$]$_4$ was synthesized as reported prior [23]. In 25 mL of DI H$_2$O, 0.426 g (1.0 mmol) of the tantalate salt is dissolved and combined with the lanthanide citrate solution in a 125 mL Teflon liner for a Parr reactor. The Parr reactor is placed in a 225 °C oven for 3 days. After cooling, the white microcrystalline product is collected via centrifugation at 4500 rpm in a Beckman-Coulter Allegra® X-22 R Centrifuge for 10 min. The top H$_2$O layer is decanted and this process is repeated for ~2–3 times with methanol to remove remaining H$_2$O, KOH, and citrate. LaTaO$_4$:Eu is formed by annealing the dry powder La$_2$Ta$_2$O$_7$(OH)$_2$:Eu in a 75 mL crucible at 900 °C for 2 h. Alternatively higher temperature annealing is carried out by pressing the dry powder La$_2$Ta$_2$O$_7$(OH)$_2$:Eu into a pellet and annealing the pellet in a 75 mL crucible at 1150 °C for 2 h.

#### 2.1.2. Solid-state synthesis of LaTaO$_4$:Eu

The reagents for these preparations included tantalum oxide, Ta$_2$O$_5$ (Acros, *FW*=441.89), europium nitrate, Eu(NO$_3$)$_3\cdot$5H$_2$O (Aldrich, *FW*=428.05) and lanthanum nitrate La(NO$_3$)$_3\cdot$6H$_2$O (Aldrich, *FW*=433.02). These were combined with alcohol (isopropanol) plus YSZ (yttria-stabilized zirconia) mixing beads in a 60 mL test tube or centrifuge tube. The alcohol-precursor slurry was then shaken on a Turbula® (General Mills Inc.) for 40–90 min. The resulting slurry mixture was poured through a Buchner funnel to remove the mixing beads, into a 75 mL crucible. The isopropanol was removed *in-vacuo* and then the powder was heated at 900 °C for 5 h. The resulting powder was remixed in the same method described above, then pressed into a pellet and heated at 1150 °C for 5 h. The pellet was reground into a powder using a mortar and pestle, remixed as described above; and again pressed into a pellet and heated at 1150 °C for 5 h: pelletization and heating were carried out a total of four times. The pellet was then ground into a fine powder for subsequent characterization. Two compositional variations were synthesized: 25%-Eu substituted LaTaO$_4$ and 30%-Eu substituted LaTaO$_4$. For both, 1 g tantalum oxide (4.5 mmol) was utilized. For the former, 0.484 g europium nitrate (1.13 mmol) and 1.469 g lanthanum nitrate (3.39 mmol) were utilized, and for the latter 0.581 g europium nitrate (1.36 mmol) and 1.372 g lanthanum nitrate (3.17 mmol) were utilized.

### 2.2. Characterization

All LaTaO$_4$:Eu were characterized by powder X-ray diffraction. X-ray powder diffraction for phase identification was performed with a Bruker D8 Advance diffractometer in Bragg–Brentano geometry with Ni-filtered Cu *K*α radiation. For samples requiring unit cell parameter refinement, the powders were mixed with Si (SRM 640c) as an internal standard prior to data collection. Lattice parameter refinement was carried out using the software package JADE (ver. 9.1). Full pattern fitting was attempted to identify the different polymorphic components; however these attempts were not successful due to poor crystallinity in the case of the materials obtained by solid-state processing, and strong preferred orientation in the case of the 'soft-chemical' materials. The Scanning Electron Microscopy and Energy Dispersive Spectroscopy (SEM-EDS) were performed on a Zeiss Supra 55VP field emission microscope equipped with an Oxford X-MAX 80 mm$^2$ detector.

The photoluminescence (PL) emission and excitation spectra were collected using a Horiba Jobin-Yvon Fluorolog-3 double-grating/double-grating Fluorescence Spectrophotometer. Powder measurements were made by orienting the sample 11° from the incident beam and detecting the emitted light from the front face of the sample. The excitation spectra were collected over the wavelength range of 250–550 nm, with the emission monitored at 614 nm. A complete instrumental correction was performed on all spectra, including corrections for the wavelength-dependent PMT response and grating efficiencies, among other factors. Absolute quantum yield measurements were made by exciting the samples with diffuse light (464 nm) inside an integrating sphere, as described prior [7,24]. Error on these measurements is ~0.6% based on prior studies [24].

## 3. Results and discussion

In our various LaTaO$_4$:Eu materials, we observe several polymorphs of LaTaO$_4$ including monoclinic $P2_1/c$ [25], orthorhombic $Cmc2_1$ [26] as well as our recently reported orthorhombic *Pbca* [7]. Fig. 1 shows representative diffraction patterns for the LaTaO$_4$:Eu formed by solid-state processing, and from annealing of the hydrothermally-obtained La$_2$Ta$_2$O$_7$(OH)$_2$:Eu precursor powder, as well as calculated diffraction patterns of the *RE*TaO$_4$ (*RE*=rare earth) polymorphs. In every case, there is 25% substitution of Eu for La, or the Eu:La ratio is 1:3. Since the calculated diffraction patterns are obtained from pure *RE*TaO$_4$ phases, they all have different *d*-spacings (thus different 2-$\theta$ peak positions) than the 25%-Eu substituted lanthanum tantalates. Therefore the observed and calculated diffraction patterns do not match, rather they are intended as a guide for polymorph identification.

We note that the LaTaO$_4$:Eu powder obtained from traditional solid-state processing possesses rather poor crystallinity, as indicated by the low signal:noise (Fig. 1a), even though it had been processed via a total of five remixing and heating steps.