A bona fide two-dimensional percolation model: an insight into the optimum photoactivator concentration in \( \text{La}_{2/3-x}\text{Eu}_x\text{Ta}_2\text{O}_7 \) nanosheets

Tadashi C Ozawa\(^1,2\), Katsutoshi Fukuda\(^2,3\), Yasuo Ebina\(^1,2\), Kosuke Kosuda\(^4\), Akira Sato\(^4\), Yuichi Michiue\(^5\), Keiji Kurashima\(^6\) and Takayoshi Sasaki\(^1,2\)

\(^1\) International Center for Materials Nanoarchitectonics, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
\(^2\) Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan
\(^3\) Collaborative Innovation Center for Nanotech FIBER, Shinshu University, 3-15-1 Tokida, Ueda, Nagano 386-8567, Japan
\(^4\) Materials Analysis Station, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
\(^5\) Quantum Beam Center, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
\(^6\) Transmission Electron Microscopy Cluster, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

E-mail: OZAWA.Tadashi@nims.go.jp

Received 13 February 2011
Accepted for publication 13 February 2011
Published 7 July 2011
Online at stacks.iop.org/STAM/12/044601

Abstract

La–Eu solid solution nanosheets \( \text{La}_{2/3-x}\text{Eu}_x\text{Ta}_2\text{O}_7 \) have been synthesized, and their photoluminescence properties have been investigated. \( \text{La}_{2/3-x}\text{Eu}_x\text{Ta}_2\text{O}_7 \) nanosheets were prepared from layered perovskite compounds \( \text{Li}_2\text{La}_{2/3-x}\text{Eu}_x\text{Ta}_2\text{O}_7 \) as the precursors by soft chemical exfoliation reactions. Both the precursors and the exfoliated nanosheets exhibit a decrease in intralayer lattice parameters as the Eu contents increase. However, there is a discontinuity in this trend between the nominal Eu content ranges \( x \leq 0.3 \) and \( x \geq 0.4 \). This discontinuity is attributed to the difference in degree of TaO\(_6\) octahedra tilting for the La- and Eu-rich phases. \( \text{La}_{2/3-x}\text{Eu}_x\text{Ta}_2\text{O}_7 \) nanosheets exhibit red emission, characteristic of the f–f transitions in Eu\(^{3+}\) photoactivators. The photoluminescence emission can be obtained from both host and direct photoactivator excitation. However, photoluminescence emission through host excitation is much more dominant than that through direct photoactivator excitation, and this behavior is consistent with that of all the other rare-earth photoactivated nanosheets reported previously. The absolute photoluminescence quantum efficiency of the \( \text{La}_{2/3-x}\text{Eu}_x\text{Ta}_2\text{O}_7 \) nanosheets increases as the experimentally determined Eu contents increase up to \( x = 0.45 \) and decrease above it. This result is in good agreement with the optimum photoactivator concentration expected from the percolation theory. These solid solution \( \text{La}_{2/3-x}\text{Eu}_x\text{Ta}_2\text{O}_7 \) nanosheets are excellent models for validating the theory of optimum photoactivator concentration in the truly two-dimensional photoactivator matrix.

Keywords: lanthanide, rare earth, layered oxide, phosphor, charge transfer
1. Introduction

Investigation of new phosphors is one of the important fields of materials research because phosphors can be used in various applications including lighting, communication, bioimaging and display devices. Phosphor research has a long history [1, 2], but it has particularly been intensified since the commercialization of blue or shorter wavelength LED, in order to search for phosphor materials that can convert emission from the LED to visible light [3, 4]. Even though numerous phosphor materials have been synthesized, new materials with higher emission efficiency are still desired for the better performance in their various applications.

Recently, a new kind of phosphor materials, which consist of rare-earth (Ln) photoactivators incorporated within the oxide nanosheet structures, have been reported and opened a new field in phosphor materials design [5–9]. The oxide nanosheets can be prepared by soft chemical exfoliation of layered compounds, and they have a unique sheet-like morphology with less than 3 nm thickness and micrometer-order lateral size [10–13]. Because of this morphology, the new oxide-nanosheet-based phosphors are quite different from conventional bulk phosphors in several aspects. Firstly, the nanosheet phosphors have a much larger surface area compared with bulk phosphors; thus, more efficient absorption of excitation energy is possible. Secondly, it is expected that various aspects of the photoluminescence properties can be tuned by appropriate modification of the surface environment through solvent exchange and surface termination with functional groups such as selected photoenergy absorbers and nonradiative energy relaxers. Thirdly, with the appropriate adjustment of concentration or viscosity, nanosheets in liquid media can be used as transparent phosphor paint, which can potentially be used to fabricate various devices by methods such as bubble-jet and screen printing [7]. Furthermore, densely packed monolayer films of such nanosheet phosphors can easily be fabricated by methods such as the Langmuir–Blodgett (LB) technique [14] and layer-by-layer deposition utilizing electrically charged polyions such as PEI (polyethylenimine) as electrostatic glue [15]. This kind of monolayer films can be combined with films of other oxide nanosheets with various functionalities, such as high-κ dielectric [16], photocatalytic [17], photochromic [18] and ferromagnetic [19] properties and metallic conductivity [20, 21], in a layer-by-layer manner in order to develop nanosheet-film-based devices. Thus, a nanosheet phosphor is one of the important functional components in such nanoarchitectonics.

When designing new phosphor materials, utilization of available theories is very important. Among them, the percolation theory for modeling the optimum photoactivator concentration is particularly important [22, 23]. In phosphors utilizing photoactivators, light is emitted from the photoactivators. Therefore, in one aspect, increasing the photoactivator concentration is required in order to enhance the emission intensity [24]. On the other hand, when the photoactivator concentration reaches a level, where energy transfer paths from photoactivators to killer (energy-trapping) centers are established through many of the neighboring photoactivators or cross relaxation of the excited energy among nearby photoactivators occurs, emission intensity decreases with the further increase in photoactivator concentration. This phenomenon is known as concentration quenching [25]. Thus, the photoactivator concentration must be optimized by balancing these two aspects in order to obtain the best emission performance from a system of interest [26, 27]. This sort of optimization can be done through experimental one-by-one characterizations of phosphor compounds with various photoactivator concentrations. However, such approach is very time consuming. To help the process, the percolation theory for modeling optimum photoactivator concentration might be applicable [28, 29]. The validity of this theory has been studied for bulk two-dimensional systems by investigating their photoluminescence properties. For those phosphors, the experimentally determined optimum photoactivator concentration agreed well with that predicted by the theory [24, 26, 30]. In general, interlayer interaction in bulk layered compounds is considered to be weak. However, it is interesting to investigate if such a theory is valid for a truly two-dimensional system with much weaker or totally negligible interlayer interactions. Because nanosheet phosphors in the form of a suspension in liquid media are separated by several orders of magnitude larger space than the adjacent layers in bulk layered compounds, nanosheet phosphor suspensions are ideal models for investigating the validity of the percolation theory for photoactivator concentration in the bona fide two-dimensional network without three-dimensional interlayer interaction.

We previously succeeded in preparing and characterizing Eu$^{3+}$-photoactivated nanosheet Eu$_{56.5}$Ta$_2$O$_7$, which was prepared by soft chemical exfoliation of the RP(Ruddlesden-Popper)-type layered-perovskite compound Li$_2$Eu$_{2/3}$Ta$_2$O$_7$ as a precursor [6]. Because the La analog of the precursor Li$_2$La$_{2/3}$Ta$_2$O$_7$ is also known to exist [31], we synthesized the La–Eu solid solution bulk precursors Li$_2$La$_{2/3}$.Eu$_{1/3}$Ta$_2$O$_7$ and exfoliated them into nanosheets. The series of resulting nanosheet phosphors with various Eu$^{3+}$-photoactivator concentrations are ideal and, to the best of our knowledge, the first models for investigating the validity of the percolation theory for photoactivator concentration in the truly two-dimensional system. Such confirmation of the validity of the theory is not only interesting for a fundamental understanding of the physical properties, but also important for the efficient development of new nanosheet-based phosphors with excellent emission properties. In this paper, we report the synthesis of La–Eu solid solution nanosheet phosphors La$_{2/3}$.Eu$_{1/3}$Ta$_2$O$_7$ and their characterization results including the photoactivator concentration dependence of the absolute photoluminescence quantum efficiency.
2. Experimental procedures

2.1. Materials

The La$_2$Ba$_{0.3-x}$Eu$_x$Ta$_2$O$_7$ nanosheets were prepared via soft chemical exfoliation of the bulk layered compounds Li$_x$La$_2$Ba$_{0.3-x}$Eu$_x$Ta$_2$O$_7$. Firstly, Li$_2$La$_2$Ba$_{0.3-x}$Eu$_x$Ta$_2$O$_7$ were prepared by solid state reactions similar to those reported previously for Li$_2$La$_2$Ta$_2$O$_7$ [31]. The starting materials of stoichiometric 2 : 0.667 : 2 Li$_2$CO$_3$ : Ln$_2$O$_3$ : Ta$_2$O$_5$ (Ln = La, Eu) and a 10% excess of Li$_2$CO$_3$, which compensates for its loss by evaporation during the heating reaction, were thoroughly mixed in an agate mortar, placed in a capped Pt crucible and heated at 1500 °C in air for 30 min and furnace-cooled to room temperature. The products consisted of melt aggregates of µm- and mm-order platelet crystals.

Secondly, Li$_2$La$_2$Ba$_{0.3-x}$Eu$_x$Ta$_2$O$_7$ were protonated by a method similar to that for preparing H$_2$La$_2$Ba$_{0.3-x}$Ta$_2$O$_7$ : nH$_2$O and H$_2$SrTa$_2$O$_7$ : nH$_2$O with some modifications [31–35]. The Li$_2$La$_2$Ba$_{0.3-x}$Eu$_x$Ta$_2$O$_7$ products were ground into powders and reacted with 2 M HNO$_3$ for 3 days at room temperature under vigorous shaking in order to exchange Li$^+$ of Li$_2$La$_2$Ba$_{0.3-x}$Eu$_x$Ta$_2$O$_7$ with H$^+$. This process was necessary in order to activate the bulk precursors for the following exfoliation process based on an acid–base reaction.

Finally, the protonated bulk precursors were reacted with a tetrabutylammonium hydroxide (TBAOH) aqueous solution. The concentration of the TBAOH solution was adjusted so that TBA$^+$ in the solution was a 3-fold excess with respect to H$^+$ in the protonated bulk precursors. After 1 week of vigorous shaking, translucent white colloidal nanosheet suspensions were obtained. These as-prepared nanosheet suspensions were centrifuged at 2500 rpm for 5 min in order to separate the unexfoliated residue as sediments and the rest of the nanosheet suspensions for characterizations.

2.2. Characterizations

Powder x-ray diffraction (XRD) patterns of the pristine and protonated bulk layered compounds were obtained using Cu Kα radiation on a Rigaku RINT2000/PC diffractometer. The diffraction peaks were indexed, and the lattice parameters were refined using APPLEMAN software [36]. The structural data of the previously reported phases Li$_2$La$_2$Ta$_2$O$_7$ and Li$_2$SrTa$_2$O$_7$ were used as the starting parameters for these processes [31, 37, 38]. However, some of the diffraction peaks of the protonated bulk precursors with the nominal Eu content $x \leq 0.3$ were very broad. Therefore, only lattice parameters $c$ along the interlayer direction were estimated from their 002 reflections for those phases. Single-crystal XRD data of a pristine bulk precursor sample were acquired at room temperature using a Bruker SMART APEXS diffractometer equipped with a graphite monochromator. The crystal was mounted on a glass fiber, and x-rays were generated using a Mo target at 50 kV and 30 mA. The crystal structure was refined utilizing SHELXL-97 software package [39]. The elemental compositions of Li$_2$La$_2$Ba$_{0.3-x}$Eu$_x$Ta$_2$O$_7$ and their protonated forms were analyzed by EPMA on a JEOL JXA-8500F using the accelerating voltage of 15 kV and beam current of 8.52 × 10$^{-5}$ mA. La$_2$P$_2$O$_7$, Eu$_2$P$_2$O$_7$ and KTaO$_3$ were used as the references for La, Eu and Ta compositions, respectively. Completion of the protonation reaction and hydration amount of the protonated bulk precursors were examined by thermogravimetric (TG) analysis on a Rigaku Thermo Plus TG8120 at a heating rate of 5 °C min$^{-1}$.

Transmission electron microscopy (TEM) observation and selected-area electron diffraction (SAED) analysis were performed on a JEOL JEM-1010 transmission electron microscope at an accelerating voltage of 100 kV for the nanosheet with the nominal Eu content $x$ = 0.60. The specimen for this characterization was prepared by dropping and drying the diluted nanosheet suspension on a carbon microgrid. The in-plane XRD patterns of La$_2$Ba$_{0.3-x}$Eu$_x$Ta$_2$O$_7$ nanosheets were obtained using the synchrotron radiation ($λ$ = 0.11979(3) nm) of the Photon Factory BL-6C at the High Energy Accelerator Research Organization (KEK). The morphology analysis of the nanosheets was performed by atomic force microscopy (AFM) using a Seiko Instruments SPA-400 AFM system with a Si tip cantilever (20 N m$^{-1}$) in the dynamic force microscopy (DFM) mode. The sample for this analysis was prepared by depositing the nanosheets on a Si substrate using a polyvinylamine-polyvinylalcohol diblock copolymer as cationic electrostatic glue [15, 20, 21, 40]. Photoluminescence excitation and emission spectra of the nanosheet suspensions were obtained using a Hitachi F-7000 fluorescence spectrophotometer at room temperature. The excitation spectra were corrected for the spectral distribution of the lamp intensity by the Rhodamine B method, and the emission spectra were corrected for the spectral response of the instrument using a substandard light source. Finally, the absolute photoluminescence quantum efficiency was measured using a Hamamatsu C9920-02 [41].

3. Results and discussion

Powder XRD profiles of the bulk precursors Li$_2$La$_2$Ba$_{0.3-x}$Eu$_x$Ta$_2$O$_7$ are shown in figure 1. The majority of reflections can be indexed based on the structure (space group P4$_2$/mm) of the previously reported La-end phase Li$_2$La$_2$Ta$_2$O$_7$ (figure 2(a)) for Li$_2$La$_2$Ba$_{0.3-x}$Eu$_x$Ta$_2$O$_7$ solid solutions with all Eu contents [31]. However, as also reported previously for the La-end phase, some relatively low-intensity reflections due to the secondary phases were also observed for all the members of Li$_2$La$_2$Ba$_{0.3-x}$Eu$_x$Ta$_2$O$_7$ [31]. These reflections were more prominent for the members with higher Eu contents.

Figure 3 shows the lattice parameters of Li$_2$La$_2$Ba$_{0.3-x}$Eu$_x$Ta$_2$O$_7$ as functions of the nominal Eu contents $x$. As described in more detail later, Li$_2$La$_2$Ba$_{0.3-x}$Eu$_x$Ta$_2$O$_7$ crystallize in the structures with space groups either P4$_2$/mm or I4/mmm depending on the Eu contents $x$. The $a$-axis of the structure with P4$_2$/mm space group is along the diagonal of the $a$–$b$–plane of the structure with I4/mmm space group. Thus, the lattice parameter $a$ of the former structure is $\sqrt{2}$ times larger than that of the latter structure. However, the lattice parameters for Li$_2$La$_2$Ba$_{0.3-x}$Eu$_x$Ta$_2$O$_7$ in
Figure 1. Powder XRD profiles of Li$_{2}$La$_{2/3-x}$Eu$_x$Ta$_2$O$_7$ for the selected nominal Eu contents $x$. The Miller indices are based on the space groups $P4_2/mnm$ and $I4/mmm$ for $x = 0$ and 0.67, respectively. Reflections that cannot be indexed based on the expected structure model are indicated with ‘*’.

Figure 2. Crystal structures of Li$_{2}$La$_{2/3-x}$Eu$_x$Ta$_2$O$_7$ for (a) $x \leq 0.3$ and (b) $x \geq 0.4$ in space groups $P4_2/mnm$ and $I4/mmm$, respectively. The structure (b) is drawn with balls-and-sticks rather than polyhedra in order to clarify the splitting of O(1) and O(3).

Figure 3. Lattice parameters of Li$_{2}$La$_{2/3-x}$Eu$_x$Ta$_2$O$_7$ (filled symbols) and their protonated forms (open symbols) as functions of the nominal Eu contents $x$. The lattice parameters $a$ along the intralayer direction and $c$ along the interlayer direction are shown in blue squares and red circles, respectively.

Figure 3 are all based on the structure with the $P4_2/mnm$ space group in order to make the comparison among the different compositions easier.

The decrease in $a$ with the increase in the Eu contents indicates that the La–Eu solid solutions were successfully prepared by controlling the relative amount of the starting materials La$_2$O$_3$ and Eu$_2$O$_3$. In contrast, $c$ increases with the increase in Eu contents. This is likely a reflection of different TaO$_6$ octahedra tilt angles depending on the amount of Eu contents as described in more detail in a later section. The continuous change in the lattice parameters was initially expected for this La–Eu solid solution system for the entire range of Eu contents. However, the result of the powder XRD indicates that there is a discontinuity in the lattice parameter trends between those with the nominal Eu contents below 0.3 and above 0.4. The structure of the La-end of the solid solution has already been well investigated by single-crystal XRD [31]. However, those of Eu-rich phases have not been studied in detail. Therefore, we examined the structure of a single-crystal sample with the nominal Eu content above 0.4 by single-crystal XRD. A small single-crystal sample with the nominal Eu content $x = 0.6$ was used for this analysis. We attempted to refine the obtained diffraction data using the structure model of the La-end phase Li$_2$La$_{2/3}$Ta$_2$O$_7$ (figure 2(a)) [31]. However, the result indicated that $wR_2^d$ from such refinement was 0.1296, which was considerably too high for the result from the structure refinement using a proper model. Thus, we attempted to refine the structure parameters using another model with the space group of $I4/mmm$, which is based on the structure of the Sr-analog Li$_2$SrTa$_2$O$_7$ (figure 2(b)) [37, 38].

The structure models with the space groups of $P4_2/mnm$ and $I4/mmm$ are compared in figure 2. Both structures consist of Ln$_2/3$Ta$_2$O$_7$ perovskite-type layers interspersed with Li$^+$. Li$^+$ is tetrahedrally coordinated with O$^{2-}$, but the tetrahedra are compressed along the interlayer direction. In addition, the adjacent perovskite-type layers are shifted by $(a+b)/2$. The main difference between the structures in $P4_2/mnm$ and $I4/mmm$ space groups is the tilting of TaO$_6$ octahedra in the perovskite-type layers. Both of the apical oxygen atoms above and below the layer are more than $4^\circ$ away from the $a$–$b$-plane normal in the case of the former structure. On the other hand, one of the apical oxygen atoms in the latter structure is perfectly aligned with the $a$–$b$-plane normal. The other apical oxygen splits into four sites with equal 1/4 occupancy within the same $a$–$b$-plane, but their average position is also along the plane normal. Thus, there is on average no tilting of TaO$_6$ octahedra in the latter structure. Because of the lack in the octahedra tilting, the latter structure has higher symmetry, and the lattice parameters $a$ and $c$ are smaller and larger than those in the former structure, respectively. Considering the lattice parameter trend in figure 3, we expect that Li$_2$La$_{2/3-x}$Eu$_x$Ta$_2$O$_7$ with the nominal Eu contents $x \geq 0.4$ all crystallize in the structure with $I4/mmm$ space.
Table 1. Crystal parameters and structure refinement data of Li$_2$La$_{2-x}$Eu$_x$Ta$_2$O$_7$.

| Crystal size       | 0.10 × 0.10 × 0.08 mm$^3$ |
|--------------------|--------------------------|
| Space group        | I4/mmm (No. 139)         |
| a (nm)             | 0.38570(1)               |
| c (nm)             | 1.8401(1)                |
| Z                  | 2                        |
| Absorption coefficient | 38.890 mm$^{-1}$     |
| $F(000)$           | 504                      |

Table 2. Atomic coordinates, site occupancy factors (SOF) and isotropic displacement parameters ($U_{iso}$ in $\AA^2$) of Li$_2$La$_{2-x}$Eu$_x$Ta$_2$O$_7$.

| Site | x  | y  | z  | SOF | $U_{iso}$ |
|------|----|----|----|-----|-----------|
| Li   | 0  | 0  | 0.25| 1   | 0.047(1)  |
| La   | 0  | 0  | 0   | 0.60| 0.0248(4) |
| Eu   | 0  | 0  | 0   | 0.07| 0.0248(4) |
| Ta   | 0  | 0  | 0.389(3)| 1 | 0.0123(2) |
| O(1) | 0  | 0.588(4) | 0.09890(11)| 0.5 | 0.037(4)  |
| O(2) | 0  | 0  | 0.2876(7)| 1  | 0.028(3)  |
| O(3) | 0  | 0.070(9)| 0.070(9)| 0.5 | 0.073(3)  |

$x$ is the amount of Eu content.

Figure 4. Powder XRD profiles of protonated Li$_2$La$_{2-x}$Eu$_x$Ta$_2$O$_7$ for the selected nominal Eu contents $x$. Very low intensity reflections that cannot be indexed based on the expected structure model are indicated with ‘*’.

The powder XRD profiles of the protonated precursors are shown in figure 4. In addition, the comparison of the lattice parameters $c$ along the interlayer direction between the pristine and protonated bulk precursors is shown in figure 3. The diffraction patterns of the protonated bulk precursors are similar to those of the pristine bulk precursors, indicating the topotactic nature of the protonation reaction. However, the 00l reflection positions, which are related to the interlayer spacing, are slightly shifted toward lower angles with respect to those of the pristine bulk precursors for $x \leq 0.3$. On the contrary, the 00l reflection positions of the protonated bulk precursors are very slightly shifted toward higher angles with respect to those of the pristine bulk precursors for $x \geq 0.4$. The similar shifts of the reflections are often observed for layered compounds after their protonation. These shifts of the reflections originate from the replacement of interlayer alkali–metal ions with protons and the hydration at the interlayer site for contraction and expansion of the interlayer spacing, respectively. Such protonation and hydration of the protonated bulk precursors were confirmed by the TG measurement as discussed in the later section. These results indicate that the protonated bulk precursors with $x \leq 0.3$ are more highly hydrated than those with $x \geq 0.4$. Differences in the shapes, positions and relative intensities, especially for the 00l reflections, between $x \leq 0.3$ and $x \geq 0.4$ suggest that the protonated precursors inherit the structural differences of their pristine precursors in those ranges. The majority of reflections can be indexed on the basis of the structure model analogous to that of Li$_2$La$_{2/3-\chi}$Eu$_\chi$Ta$_2$O$_7$ (space group I4/mmm) for $x \geq 0.4$. However, the lattice parameter trend of the protonated bulk precursors is not as clear as that of the pristine bulk precursors. The lack of the clear Eu-content dependence of the lattice parameters in the protonated series might be due to their different degrees of TaO$_6$ octahedra tilting. In the diffraction profiles of the protonated bulk precursors, some very low intensity reflections, which cannot be indexed, were also observed. The intensities of those reflections were higher for those with higher Eu contents, although they were observed for all the members of the protonated Li$_2$La$_{2/3-\chi}$Eu$_\chi$Ta$_2$O$_7$. We believe that those reflections are mainly due to the secondary phases remaining even after the protonation reactions. On the contrary, indexing of the...
diffraction peaks of the protonated bulk precursors with $x \leq 0.3$ is difficult owing to the broadness of the peaks. The protonated Li$_2$La$_{2/3}$Ta$_2$O$_7$ is known to hydrate and dehydrate reversibly [33]. Thus, the broad diffraction profiles of the protonated Li$_2$La$_{2/3}$–x Eu$_x$Ta$_2$O$_7$ are likely due to the coexistence of hydrated phases with different amount of hydration. In addition, stacking faults of the layers of the protonated bulk precursors might be causing the peak broadening up to $x = 0.4$ just like the stacking faults observed in the Sr-analog H$_2$SrTa$_2$O$_7$·nH$_2$O [37].

Progress of the protonation of Li$_2$La$_{2/3}$–x Eu$_x$Ta$_2$O$_7$ was also investigated by TG analysis using a protonated sample with the nominal Eu content $x = 0.60$, and the result is shown in figure 5. The first weight loss up to 100 °C is attributed to the loss of hydrated water, and the second weight loss above 100 °C is attributed to the deprotonation and the simultaneous oxygen loss. These two-step weight losses are typical for protonated layered oxides [5–8]. In the case of RP-type protonated tantalates, these thermal reactions can be expressed in the following idealized chemical equations:

$$\text{H}_2\text{Ln}_{2/3}\text{Ta}_2\text{O}_7 \cdot n\text{H}_2\text{O} \rightarrow \text{H}_2\text{Ln}_{2/3}\text{Ta}_2\text{O}_7 + n\text{H}_2\text{O},$$

$$\text{H}_2\text{Ln}_{2/3}\text{Ta}_2\text{O}_7 \rightarrow 2\text{Ln}_{1/3}\text{Ta}_3\text{O}_5 + \text{H}_2\text{O}.$$  

Assuming that a sample is single phase, hydration and protonation amounts can be estimated from the weight loss. The estimated chemical formula for the protonated sample with the nominal Eu content $x = 0.60$ is H$_{0.87}$La$_{0.07}$Eu$_{0.60}$Ta$_2$O$_7$·0.04H$_2$O, which indicates that the majority of Li$^+$ was successfully exchanged with H$^+$. Based on the charge balance in the system, 2 of H$^+$ per formula are expected. In a related layered perovskite KLnNb$_2$O$_7$ and some other systems, a small amount of alkali–metal ions are known to remain after the similar protonation reactions [5]. Considering this fact, it is rational to expect that a small amount of Li$^+$ ions are also remaining in the interlayer site of the current system as Li$_{0.13}$H$_{1.87}$La$_{0.07}$Eu$_{0.60}$Ta$_2$O$_7$·0.04H$_2$O. In addition, possible oxygen deficiencies produced after the protonation reactions might be causing the smaller amount of estimated H$^+$ than the expected amount. Powder XRD of the protonated sample heated up to 1000 °C for this TG analysis was taken. The result in figure 6 indicates that the majority phase in this product is Ln$_{1/3}$Ta$_3$O$_5$ perovskite, and no sign of reflections from Li-containing phase was observed. This result also indicates that the majority of Li$^+$ in Li$_2$Ln$_{2/3}$Ta$_2$O$_7$ was successfully exchanged with H$^+$ by the protonation reactions, and the amount of residual Li$^+$ must be small.

Elemental compositions of La, Eu and Ta in Li$_2$La$_{2/3}$–x Eu$_x$Ta$_2$O$_7$ and their protonated forms were examined by EPMA, and the results are summarized in table 3 and figure 7. La and Eu contents change linearly with respect to the nominal Eu contents $x$. The La and Eu contents in the pristine Li-phases correspond well with the stoichiometric amount of the starting materials used. However, protonated phases have lower La and Eu contents than those in the pristine Li-phases and those expected from the amounts of the starting materials used. The amount of the site deficiency is minor for La, but it is significant for Eu. The estimated Eu content in the sample with the nominal Eu content $x = 0.67$ is as low as 0.56, which is about 20% less than that expected from the amount of Eu in the starting materials. This indicates that La and Eu were extracted from the perovskite-type layers of the bulk precursors during the protonation processes, and Eu is more preferentially extracted than La by the acid treatment. The elemental compositions in oxide nanosheets prepared by soft chemical approaches generally inherit those in the layer unit of their precursors. Thus, we expect that the actual La and Eu contents in the La$_{2/3}$–x Eu$_x$Ta$_2$O$_7$ nanosheets prepared in this study also correspond to those in the protonated precursors in table 3. If there were no extraction of Ln by the acid treatment, the

![Figure 5](image1.png)

**Figure 5.** TG analysis result of the protonated Li$_2$La$_{0.07}$Eu$_{0.60}$Ta$_2$O$_7$ sample.

![Figure 6](image2.png)

**Figure 6.** Powder XRD profile of the protonated Li$_2$La$_{0.07}$Eu$_{0.60}$Ta$_2$O$_7$ sample heated up to 1000 °C for the TG analysis.

| Table 3. Elemental composition analysis results of Li$_2$La$_{2/3}$–x Eu$_x$Ta$_2$O$_7$ and their protonated forms by EPMA.  
Nominal Eu content $x$ | Mole ratio of elements in Li-phase | Mole ratio of elements in H-phase |
|-----------------------|----------------------------------|----------------------------------|
| 0                     | 0.63 0 2.00 0.58 0 2.00          | 0.63 0 2.00 0.58 0 2.00          |
| 0.10                  | 0.55 0.07 2.00 0.52 0.08 2.00    | 0.55 0.07 2.00 0.52 0.08 2.00    |
| 0.20                  | 0.46 0.22 2.00 0.43 0.15 2.00    | 0.46 0.22 2.00 0.43 0.15 2.00    |
| 0.30                  | 0.38 0.32 2.00 0.33 0.23 2.00    | 0.38 0.32 2.00 0.33 0.23 2.00    |
| 0.40                  | 0.27 0.42 2.00 0.27 0.30 2.00    | 0.27 0.42 2.00 0.27 0.30 2.00    |
| 0.50                  | 0.18 0.52 2.00 0.17 0.38 2.00    | 0.18 0.52 2.00 0.17 0.38 2.00    |
| 0.60                  | 0.09 0.61 2.00 0.06 0.45 2.00    | 0.09 0.61 2.00 0.06 0.45 2.00    |
| 0.67                  | 0 0.71 2.00 0 0.56 2.00         | 0 0.71 2.00 0 0.56 2.00         |

The values are normalized to 2 of Ta as in the nominal chemical formula A$_2$La$_{2/3}$–x Eu$_x$Ta$_2$O$_7$.  

Sci. Technol. Adv. Mater. 12 (2011) 044601  
T C Ozawa et al
charge of the La$_{2/3-x}$Eu$_x$Ta$_2$O$_7$ nanosheet would be 2$^-$ because these nanosheets were formed by losing 2 of A$^+$ from the neutral A$_2$La$_{2/3-x}$Eu$_x$Ta$_2$O$_7$ ($A = Li$, H) precursors. Considering the fact that some amount of Ln was lost during the protonation reactions to prepare the nanosheets in this study, the charge of the nanosheet would be more negative than 2$^-$, However, no such increase in negative charge in the layer unit has been observed for other oxide nanosheets prepared by similar soft chemical reactions. Another possibility is that the total charge of the nanosheets is maintained approximately at 2$^-$ owing to the simultaneous extraction of Ln$^{3+}$ and O$^{2-}$ from the layer units of the precursors during the acid treatment. In order to simplify the expressions for the nanosheet products in this study, the nanosheet prepared from the precursor with the nominal Eu content $x$ is denoted as Eu($x$)-nanosheet below.

These protonated layered oxide precursors were reacted with TBAOH aqueous solutions in order to exfoliate them into nanosheets. Figure 8 shows the aqueous suspension of Eu($0.60$)-nanosheets as a typical example. It is translucent and exhibits the Tyndall effect by the scattering of a laser beam because of its colloidal nature. The nanosheet suspensions of all the other Eu contents have lateral sizes ranging from 0.2 to 2 $\mu$m. The thickness of the nanosheets is uniformly 2.0(2) $\mu$m. This thickness is larger than that expected from the ideal crystal structure of Li$_2$Ln$_{2/3}$Ta$_2$O$_7$ layered perovskite (1.07 nm) [6, 31]. However, the thicknesses of other kind of nanosheets prepared by the similar manner also tend to be larger than expected due to species, such as H$_2$O and TBA$^+$, existing on the surface of the nanosheets. Thus, the uniform-thickness of the Eu($x$)-nanosheets prepared in this study is an indication of their homogeneously unilamellar nature.

Figure 11 shows the TEM image (panel a) and SAED pattern (panel b) of Eu($0.60$)-nanosheets. The majority of the observed nanosheets have lateral sizes ranging from 0.2 to 2 $\mu$m consistent with the AFM observation results. The exceedingly faint and monotonic contrast of the sheet images reflects the ultrathin nature and uniform thickness of the unilamellar nanosheets. The SAED pattern of a single nanosheet exhibits intense diffraction spots indicating the single crystalline nature of the nanosheet. Similarly to the in-plane XRD pattern of the nanosheets, the diffraction spots of the single nanosheet were indexed well to the square-type cell where no difference in two of the orthogonal lattice parameters along the in-sheet directions ($a$- and $b$-axes) was observed within the experimental resolution limit. The estimated lattice parameter of the nanosheet along the in-sheet direction is $a = 0.39$ nm, which is very close to those (or the square roots of those in cases where diagonal cells are more appropriate for their symmetry) of the bulk precursors and the result of the in-plane XRD. These results also suggest that the exfoliation reaction is topotactic and the nanosheet products retain the perovskite-type layer structure of their bulk precursors.

The red emission from these nanosheets is intense enough that it can be visually confirmed when the nanosheet suspensions are irradiated by UV light (figure 12a inset). Photoluminescence excitation and emission spectra of the
Eu(x)-nanosheet suspensions are shown in figure 12. The emission spectra of the nanosheets with different Eu contents are basically the same except for the difference in the intensities. Several peaks were observed in the emission spectra. These peaks are attributed to the intra-4f transitions of Eu$^{3+}$ photoactivators [5–7]. The emission intensities increase as the nominal Eu contents increase up to $x = 0.60$ and decrease above it. The excitation spectra monitored at 616 nm consist of trace-level peaks around 400 nm and a predominant broad peak below 350 nm. The former is attributed to the intra-4f excitation transitions of Eu$^{3+}$ photoactivators, and the latter is attributed to the host excitation. To the best of our knowledge, all the previously reported Ln$^{3+}$-photoactivated nanosheets also exhibited the similar excitation behavior where the emission through host excitation was more predominant than that through direct Ln$^{3+}$-photoactivator excitation [5–8]. Thus, this behavior is considered to be characteristic of the Ln$^{3+}$-photoactivated nanosheets, and related to the very large surface and/or large absorption cross-section of the nanosheets. The wavelengths of these host excitation peaks are much longer than those of their absorption edges around 250 nm. Considering this result and the photoluminescence properties of many of the previously reported Eu$^{3+}$-photoactivated oxides, the origin of these peaks is attributed to the O$^{2–}$–Eu$^{3+}$ charge-transfer transition rather than the band gap excitation [46–50]. The excitation maxima of the nanosheets shift to a shorter wavelength as their Eu$^{3+}$ contents decrease. Similarly, the nanosheets with higher Eu$^{3+}$ contents have shorter O$^{2–}$–Eu$^{3+}$ distances (estimated from the lattice parameters). According to Hoefdraad, the position of the charge-transfer band is, in general, determined by the O$^{2–}$–Eu$^{3+}$ distance where the band shifts to lower energy with the increase in the bond length [51]. Thus, the relationship between the O$^{2–}$–Eu$^{3+}$ distances and the charge-transfer band positions in the Eu(x)-nanosheets is contrary to the general trend. In the case of the Eu(x)-nanosheets, the amount of the Ln-site deficiencies increases with the increase in the Eu contents. These deficiencies might be contributing to the unusual trend in the charge-transfer band positions. The highest emission intensity was observed for Eu(0.60)-nanosheets among the as-prepared nanosheet products by photoluminescence spectra measurements. The more quantitative comparison of the photoluminescence performance of these nanosheets with various Eu$^{3+}$-photoactivator concentrations was made by the absolute photoluminescence quantum efficiency measurements.

The absolute photoluminescence quantum efficiency of the nanosheet suspensions as a function of the nominal Eu contents $x$ obtained by exciting at 276 nm is plotted in figure 13. The photoluminescence quantum efficiency increases up to the nominal Eu content $x = 0.6$ and then decreases above it. The relatively smooth trend in $0.2 < x < 0.6$ indicates that the slight difference in the TaO$_x$-octahedra tilting among the La- and Eu-rich nanosheets does not have a significant effect on the photoluminescence quantum efficiency, and the Eu$^{3+}$ concentration is the dominant factor affecting the quantum efficiency.
The relationship between the optimum photoactivator concentrations $x_c$ and the emission intensity/efficiency are often investigated using the percolation theory [30, 52–54]. The percolation theory for phosphor materials is based on the establishment of energy transfer paths from photoactivators to killer centers or cross relaxation of excited energy among nearby photoactivators. In general, the killer centers originate from factors such as photoactivator-site deficiency and defects in other parts of the host structure. In the Eu($x$)-nanosheet system, 1/3 of the Ln$^{3+}$-photoactivator site is intrinsically unoccupied, and the additional site deficiency tends to increase as the Eu contents increase. Also, the luminescence intensity increases as the Eu contents increase for the most parts of the system. These properties of the Eu($x$)-nanosheets suggest that the photoactivator-site deficiency is not significantly acting as the killer centers in this system even though the true nature of the killer centers in this system is not understood at this stage.

Based on the percolation theory, $x_c$ can be approximated in the expression as $x_c = d/[(d - 1) \cdot z]$ where $z$ is the number of interacting neighbor photoactivator sites and $d$ is the dimensionality of the percolation lattice [22]. Previously, various bulk layered oxides with Ln$^{3+}$-photoactivators were investigated to confirm the validity of this model for bulk two-dimensional systems [24, 26, 30]. The experimentally determined $x_c$ of those bulk layered oxides corresponded well with those estimated from the percolation theory. In general, the interlayer interactions are considered to be weak compared with the intralayer interactions in those layered bulk compounds. However, investigations of the two-dimensional system with truly no interlayer interaction are more interesting and important to understand the fundamentals of the energy transfer within the two-dimensional photoactivator network. For this aspect, the Eu($x$)-nanosheets are ideal models because the interlayer spacing of the nanosheets in the form of aqueous suspensions is several orders of magnitude larger than those in the bulk layered compounds. In the case of the Eu($x$)-nanosheets, $z = 4$ and $d = 2$; thus, the optimum photoactivator concentration estimated by the percolation theory is $x_c = 0.5$. Two assumptions are made for this estimation. Firstly, the Eu$^{3+}$-photoactivator interactions are only among the nearest neighbors in the Ln-sites of the host lattice. Secondly, the origin of the concentration quenching is the energy migration from Eu$^{3+}$ photoactivators to killer centers or cross relaxation. Because of the lower dimensionality ($d = 2$), the values of $x_c$ in two-dimensional systems are much higher than those in three-dimensional systems [26, 30, 52–54]. This relatively high $x_c$ is an advantage for the two-dimensional systems to allow incorporating an unusually high number of photoactivators without concentration quenching [30]. The theoretical $x_c$ of the Eu($x$)-nanosheets agrees very well with that determined experimentally $x_c = 0.45$ ($x = 0.60$ nominal), considering the accuracy of the elemental compositions estimated by EPMA [55]. This result suggests that the percolation theory reasonably models the energy transfer process within the truly two-dimensional photoactivator network, and the assumptions made for the model are valid. If the photoactivator interaction were through a super-exchange mechanism, the next-nearest-neighbor interaction would have to be taken into account because the next-nearest neighbors would interact through the central O$^{2-}$ ion [55]. However, the estimated value of $x_c$ in such a case would be too
small compared with the experimentally determined value because of the increase in $z$ in such a model. Thus, the photoactivator interaction in the Eu(x)-nanosheets must be mainly through a direct multipole–multipole mechanism [24, 26, 30]. In addition, the percolation theory is a static model, whereas the energy migration is a dynamic process. The time-dependent factor in the actual energy transfer process might have some effect on the optimum photoactivator concentrations. However, considering the close agreement between the experimentally and theoretically determined $z_c$, the contribution from such a factor must be small [30, 53].

4. Conclusion

We have prepared the solid solutions Li$_2$La$_{2/3-z}$Eu$_z$Ta$_2$O$_7$ and exfoliated them into unilamellar nanosheets. These nanosheets consist of a two-dimensional network of Eu$^{3+}$ photoactivators. Because the distance between the neighboring nanosheets in the suspensions is several orders of magnitude larger than the interlayer distances in the bulk layered compounds, these nanosheets are considered as the bona fide two-dimensional network of the photoactivators. To the best of our knowledge, this is the first report on the investigation of the optimum photoactivator concentration in the truly two-dimensional network based on their absolute photoluminescence quantum efficiency measurements. These results confirm the validity of the percolation theory for the truly two-dimensional network. Theoretical prediction of the photoluminescence quantum efficiency is very important for the design of new phosphors, and this validation of the percolation theory on the photoactivator concentrations provides more reliable utilization of the theory in the efficient design of high performance phosphor materials.

Acknowledgments

This work was supported by World Premier International Research Center (WPI) Initiative on Materials Nanoarchitectonics, MEXT, Japan, and CREST of the Japan Science and Technology Agency (JST). The schematic crystal structure shown in figure 2 was drawn with ‘Balls and Sticks’, free software for crystal structure visualization [56].

References

[1] Žukauskas A, Shur M S and Gaska R 2002 Introduction to Solid-State Lighting (New York: Wiley-Interscience)
[2] Shionoya S and Yen W M (ed) 1999 Phosphor Handbook (Boca Raton, FL: CRC Press)
[3] Nakamura S, Senoh M and Mukai T 1993 Japan. J. Appl. Phys., Part 2 32 L8
[4] Nakamura S, Mukai T and Senoh M 1994 Appl. Phys. Lett. 64 1687
[5] Ozawa T C, Fukuda K, Akatsuka K, Ebina Y and Sasaki T 2007 Chem. Mater. 19 6675
[6] Ozawa T C, Fukuda K, Akatsuka K, Ebina Y, Sasaki T, Kurashima K and Kosuda K 2008 J. Phys. Chem. C 112 1312
[7] Ozawa T C, Fukuda K, Akatsuka K, Ebina Y, Sasaki T, Kurashima K and Kosuda K 2008 J. Phys. Chem. C 112 17115
[8] Ozawa T C, Fukuda K, Akatsuka K, Ebina Y, Kurashima K and Sasaki T 2009 J. Phys. Chem. C 113 8735
[9] Ida S, Ogata C, Eguchi M, Youngblood W J, Mallouk T E and Matsumoto Y 2008 J. Am. Chem. Soc. 130 7052
[10] Sasaki T, Watanabe M, Hashizume H, Yamada H and Nakazawa H 1996 Chem. Commun. 229
[11] Sasaki T, Watanabe M, Hashizume H, Yamada H and Nakazawa H 1996 J. Am. Chem. Soc. 118 8329
[12] Sasaki T and Watanabe M 1998 J. Am. Chem. Soc. 120 4682
[13] Sasaki T 2007 J. Ceram. Soc. Japan 115 9
[14] Muramatsu M, Akatsuka K, Ebina Y, Wang K, Sasaki T, Ishida T, Miyake K and Haga M 2005 Langmuir 21 6590
[15] Sasaki T, Ebina Y, Watanabe M and Decher G 2000 Chem. Commun. 2163
[16] Osada M, Ebina Y, Funakubo H, Yokoyama S, Kiguchi T, Takada K and Sasaki T 2006 Adv. Mater. 18 1023
[17] Ebina Y, Sakai N and Sasaki T 2005 J. Phys. Chem. B 109 17212
[18] Fukuda K, Akatsuka K, Ebina Y, Ma R, Takada K, Nakai I and Sasaki T 2008 ACS Nano 2 1689
[19] Osada M, Ebina Y, Fukuda K, Ono K, Takada K, Yamaura K, Takayama-Muramachi E and Sasaki T 2006 Phys. Rev. B 73 153301
[20] Fukuda K, Kato H, Sugimoto W and Takasu Y 2009 MRS Fall Meeting Vol. 1109 (Boston, MA: Materials Research Society) p 98
[21] Sato J, Kato H, Kimura M, Fukuda K and Sugimoto W 2010 Langmuir 26 18049
[22] Vyssotsky V A, Gordon S B, Frisch H L and Hammersley J M 1961 Phys. Rev. 123 1566
[23] Van Uitert L G, Linares R C, Soden R R and Ballman A A 1962 J. Chem. Phys. 36 702
[24] Homma T, Toda K, Ye Z-G and Sato M 1998 J. Phys. Chem. Solids 59 1187
[25] Botden T P J 1952 Philips Res. Rep. 7 197
[26] Toda K, Kameo Y, Ohta M and Sato M 1995 J. Alloys Compd. 218 228
[27] Van Uitert L G and Iida S 1962 J. Chem. Phys. 37 986
[28] Dexter D L and Schulman J H 1954 J. Chem. Phys. 22 1063
[29] Blassie G 1978 Luminescence of Inorganic Solids ed B Di Bartolo (New York: Plenum) p 457
[30] Toda K, Homma T and Sato M 1997 J. Lumin. 71 71
[31] Crosnier-Lopez M-P, Le Berre F and Fourquet J-L 2002 Z. Anorg. Allg. Chem. 628 2049
[32] Shimizu K I, Itoh S, Hatamachi T, Kitayama Y and Kodama T 2006 J. Mater. Chem. 16 773
[33] Le Berre F, Crosnier-Lopez M-P and Fourquet J-L 2006 Mater. Res. Bull. 41 825
[34] Bhuvanesh N S P, Crosnier-Lopez M-P, Duroy H and Fourquet J-L 2000 J. Mater. Chem. 10 1685
[35] Crosnier-Lopez M-P, Le Berre F and Fourquet J-L 2001 J. Mater. Chem. 11 1146
[36] Applemann D E and Evans H T J 1973 PB National Technical Information: Springfield, VA, p 60
[37] Crosnier-Lopez M-P and Fourquet J-L 2005 Solid State Sci. 7 530
[38] Pagnier T, Rosman N, Galven C, Suard E, Fourquet J L, Le Berre F and Crosnier-Lopez M P 2009 J. Solid State Chem. 182 317
[39] Sheldrick G M 1997 SHELXTL version 6.10 (Madison, WI: Bruker AXS Inc.)
[40] Fukuda K, Nakai I, Ebina Y, Tanaka M, Mori T and Sasaki T 2006 J. Phys. Chem. B 110 17070
[41] Suzuki K, Kobayashi A, Kaneko S, Takehira K, Yoshihara T, Ishida H, Shiina Y, Oishi S and Tobita S 2009 Phys. Chem. Chem. Phys. 11 9850
[42] Goldschmidt V M 1926 Skr. Norske Vidensk. Akad. No. 2
[43] Johnsson M and Lemmens P 2008 J. Phys.: Condens. Matter 20 264001
[44] Yakel H Jr 1955 Acta Crystallogr. 8 394
[45] Geller S 1957 Acta Crystallogr. 10 248
[46] Bizeto M A, Constantino V R L and Brito H F 2000 J. Alloys Compd. 311 159
[47] Chang N C 1963 J. Appl. Phys. 34 3500
[48] Blasse G and Bril A 1968 J. Chem. Phys. 48 3652
[49] Blasse G 1966 J. Chem. Phys. 45 2356
[50] Ferdov S, Sá Ferreira R A and Lin Z 2006 Chem. Mater. 18 5958
[51] Hoefdraad H E 1975 J. Solid State Chem. 15 175
[52] Ozawa L and Jaffe P M 1971 J. Electrochem. Soc. 118 1678
[53] Keyes T and Pratt S 1979 Chem. Phys. Lett. 65 100
[54] Yonezawa F, Sakamoto S and Hori M 1989 Phys. Rev. B 40 636
[55] Berdowski P A M and Blasse G 1986 J. Solid State Chem. 63 86
[56] Ozawa T C and Kang S J 2004 J. Appl. Crystallogr. 37 679