Preparation and Photoluminescence Characterizations of Eu^{3+}-doped Oxide Nanosheets

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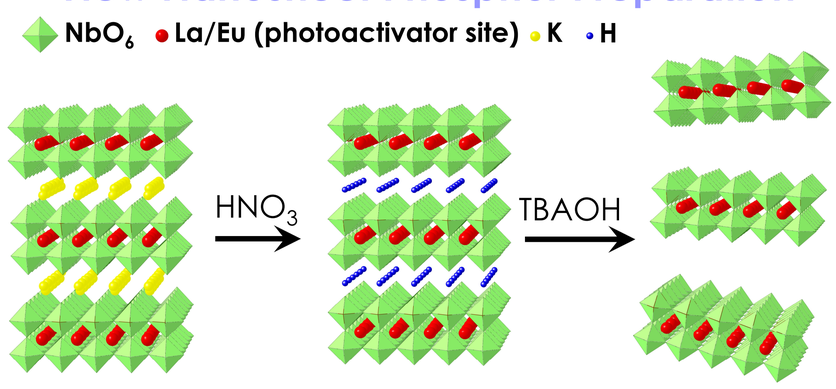
Introduction

Most of the previously reported Ln-activated nanosheet-based phosphors consist of Ln ions or Ln-containing complexes inserted between transition metal oxide nanosheets. The photoluminescence properties of these internanosheet-site activated phosphors tend to be quite susceptible to the amount of cointercalated species, such as H_2O and hydronium ions, which act as energy-transfer mediators. In addition, more efficient energy transfer from the host nanosheet unit to the photoactivators is expected if the activators are incorporated in intrananosheet sites rather than in internanosheet sites. Thus, we have prepared new types of nanosheet-based phosphors which consist of perovskite-type oxide nanosheets with Eu^{3+} photoactivator doped in the intrananosheet site, and their properties have been characterized.

Nanosheet Phosphor Preparation by Soft Chemical Topotactic Exfoliation

(ex. $La_{0.90}Eu_{0.05}Nb_2O_7$ nanosheet)

New Nanosheet Phosphor Preparation

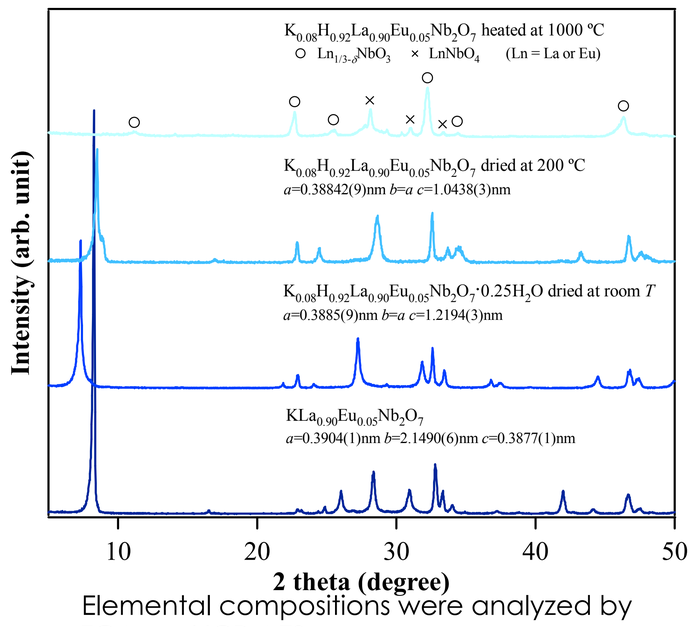


$KLa_{0.90}Eu_{0.05}Nb_2O_7$
Using K_2CO_3, La_2O_3, Eu_2O_3 and Nb_2O_5 as staring materials, this bulk precursor was prepared by solid state reaction.

$K_{1-x}H_xLa_{0.90}Eu_{0.05}Nb_2O_7$
K of the bulk precursor was ion exchanged with H in order to activate the bulk precursor for the following soft chemical exfoliation reaction.

$La_{0.90}Eu_{0.05}Nb_2O_7$ nanosheet
The protonated bulk precursor has been reacted with TBAOH to exfoliate it into nanosheets.

Powder X-ray Diffraction of Bulk Precursors

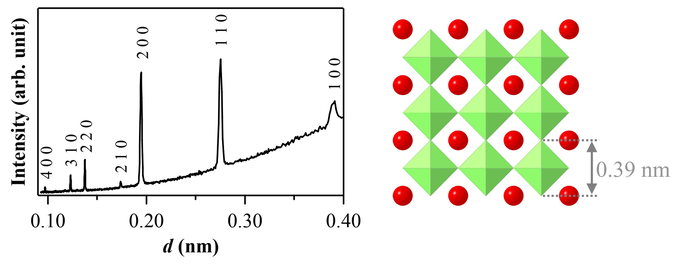


Elemental compositions were analyzed by TGA and ICP-AES.

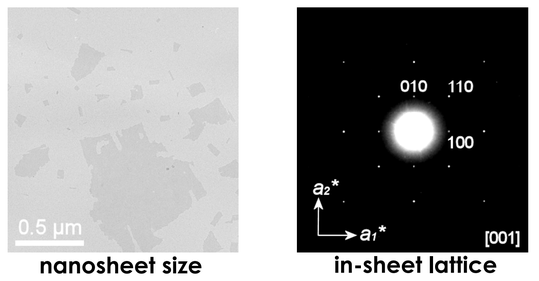
Morphology and Single-crystalline Nature of Nanosheet Phosphors

(ex. $La_{0.90}Eu_{0.05}Nb_2O_7$ nanosheet)

In-plane X-ray Diffraction



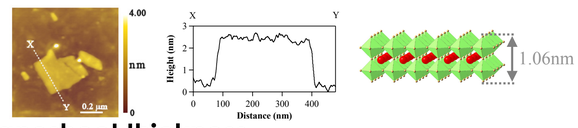
TEM Observation



nanosheet size
0.1~1 μm

in-sheet lattice
tetragonal a = 0.4 nm

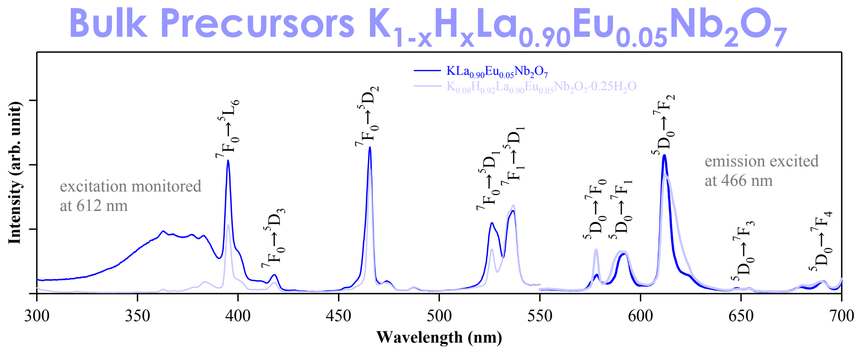
AFM Observation



nanosheet thickness
Observed by AFM: 2.01(1) nm
Estimation from crystallographic data: 1.06 nm
⇒ possible adsorption of oxonium and TBA^+ ions, and other uncertain factors

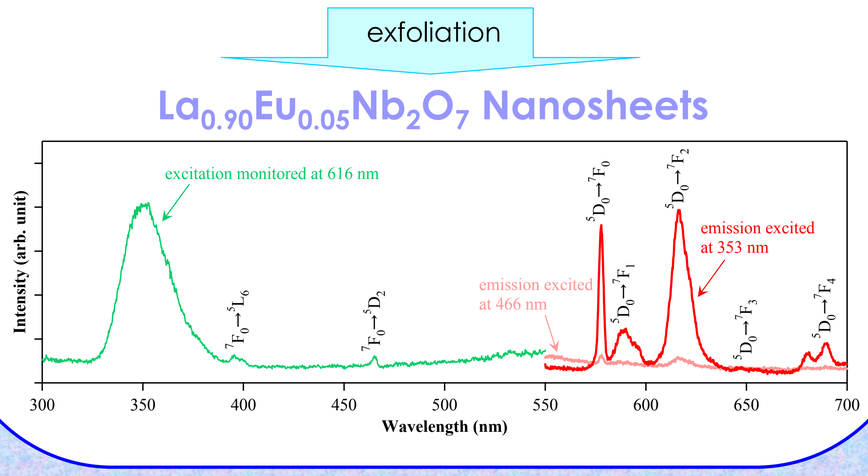
Photoluminescence Properties of Layered Oxides Before and After Exfoliation

Bulk Precursors $K_{1-x}H_xLa_{0.90}Eu_{0.05}Nb_2O_7$



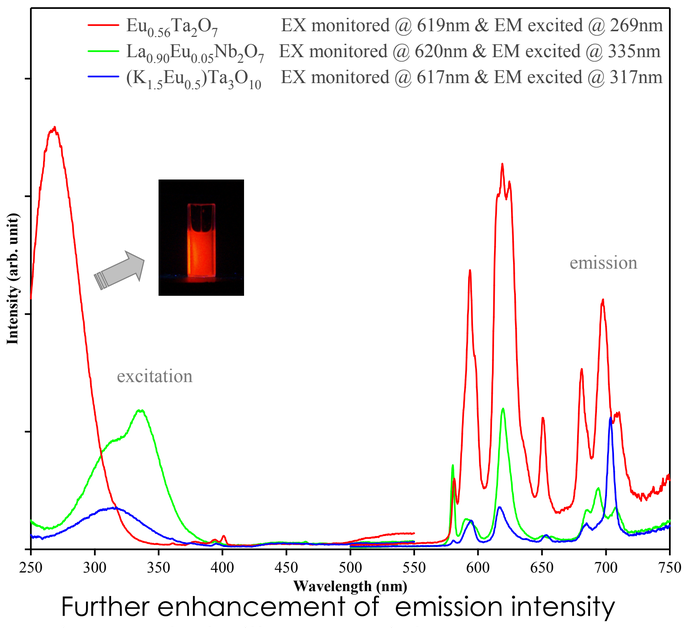
exfoliation

$La_{0.90}Eu_{0.05}Nb_2O_7$ Nanosheets



Photoluminescence of Different Nanosheet Phosphors

(5.2 × 10^{-4} M suspensions)

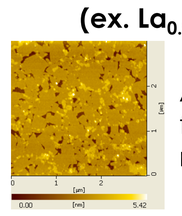


Further enhancement of emission intensity is expected with appropriate photoactivator-concentration adjustments.

Practical Aspects

Film Fabrication

(ex. $La_{0.90}Eu_{0.05}Nb_2O_7$ nanosheet)



A monolayer film can easily be fabricated by Langmuir-Blodgett method.

Nanosheet Phosphor Paint

(ex. $(K_{1.5}Eu_{0.5})Ta_3O_{10}$ nanosheet)

Nanosheet suspension concentrated by high-speed (~20000 rpm) centrifugation is viscous enough that it can be painted on a material such as glass without being shed.

under room light

under UV irradiation in a darkroom

Conclusion

- The novel intrananosheet site activated phosphors $La_{0.90}Eu_{0.05}Nb_2O_7$, $Eu_{0.56}Ta_2O_7$ and $(K_{1.5}Eu_{0.5})Ta_3O_{10}$ have been prepared, and their photoluminescence properties have been characterized.
- These nanosheets exhibit photoluminescence emission from the $^5D_0$ to ^7F_J manifold transitions of Eu^{3+} by either direct excitation of Eu^{3+} or host excitation.
- These intrananosheet site activated phosphors exhibit effective energy transfer from the nanosheet hosts to Eu^{3+} on the contrary to the direct excitation dominated photoluminescence emission of their bulk precursors.

Acknowledgement

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