Optical Properties for New Noncentrosymmetric Sodium Lanthanide Iodates, $NaLn(IO_3)_4$ (Ln = La, Ce, Sm, and Eu)

Seung-Jin Oh, Hyung Gu Kim, and Kang Min Ok*

Department of Chemistry, Chung-Ang University, Seoul 06974, Republic of Korea.

Abstract

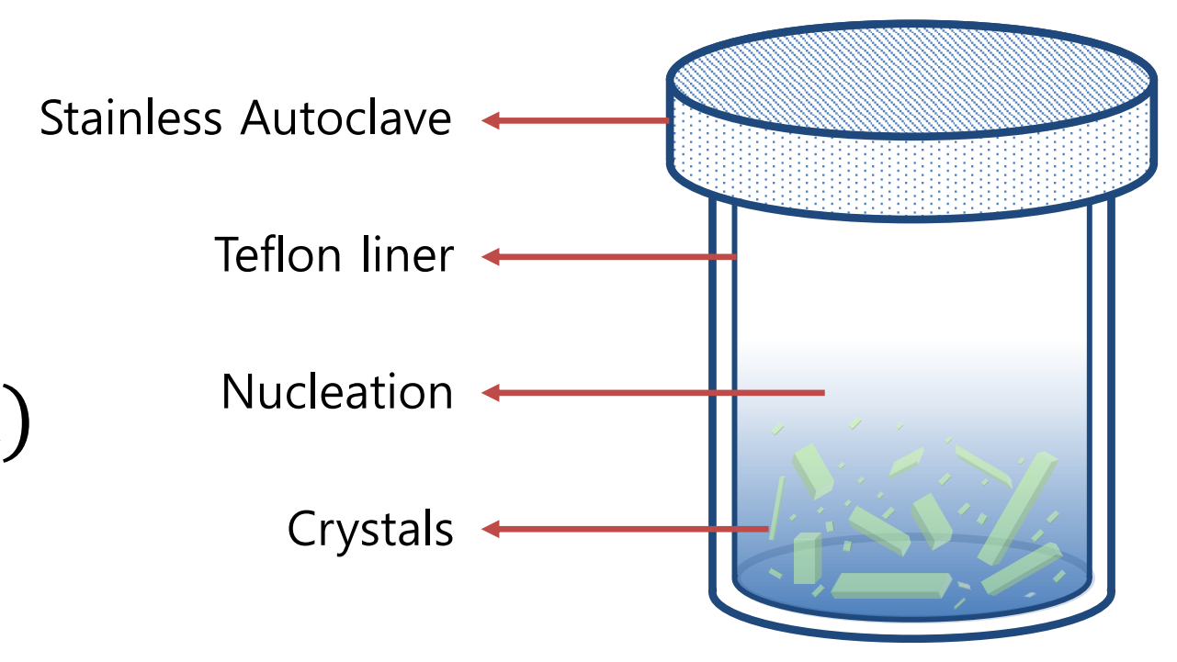
Crystals of four isostructural iodates, $NaLn(IO_3)_4$ (Ln = La, Ce, Sm, and Eu), have been synthesized through hydrothermal reactions. The single-crystal X-ray diffraction (SCXRD) reveals that the materials crystalize in the acentric monoclinic space group, *Cc* (No. 9). The crystals have two-dimensional structures where the sheets are parallel along the *a*-axis. The layers consist of lanthanide cations coordinated by eight-O atoms of iodate groups leading to anionic frameworks. The Na^+ cations act as intra-layer cations to balance the anionic frameworks of the eight-membered-ring channels directed to the (010) plane. Close structure investigation suggests that since the constructive sum of the dipole moments of iodates, the compounds reveal type-I phase matching behavior with strong second harmonic generation (SHG) efficiency of ca. 100 times that of α-SiO_2. In addition, photoluminescence (PL) properties were also investigated for Eu-compounds and Ce^{3+}, Sm^{3+} and Eu^{3+} doped-$NaLa(IO_3)_4$ at various temperatures. The phenomenon that the transition of electric dipole is stronger than that of magnetic dipole was observed in the PL emission spectra for Sm^{3+} and Eu^{3+}, which confirms that the environment of the materials is asymmetric. Infrared, UV-vis spectroscopy, thermal analyses, and their dipole moment calculations are also investigated.

Synthesis

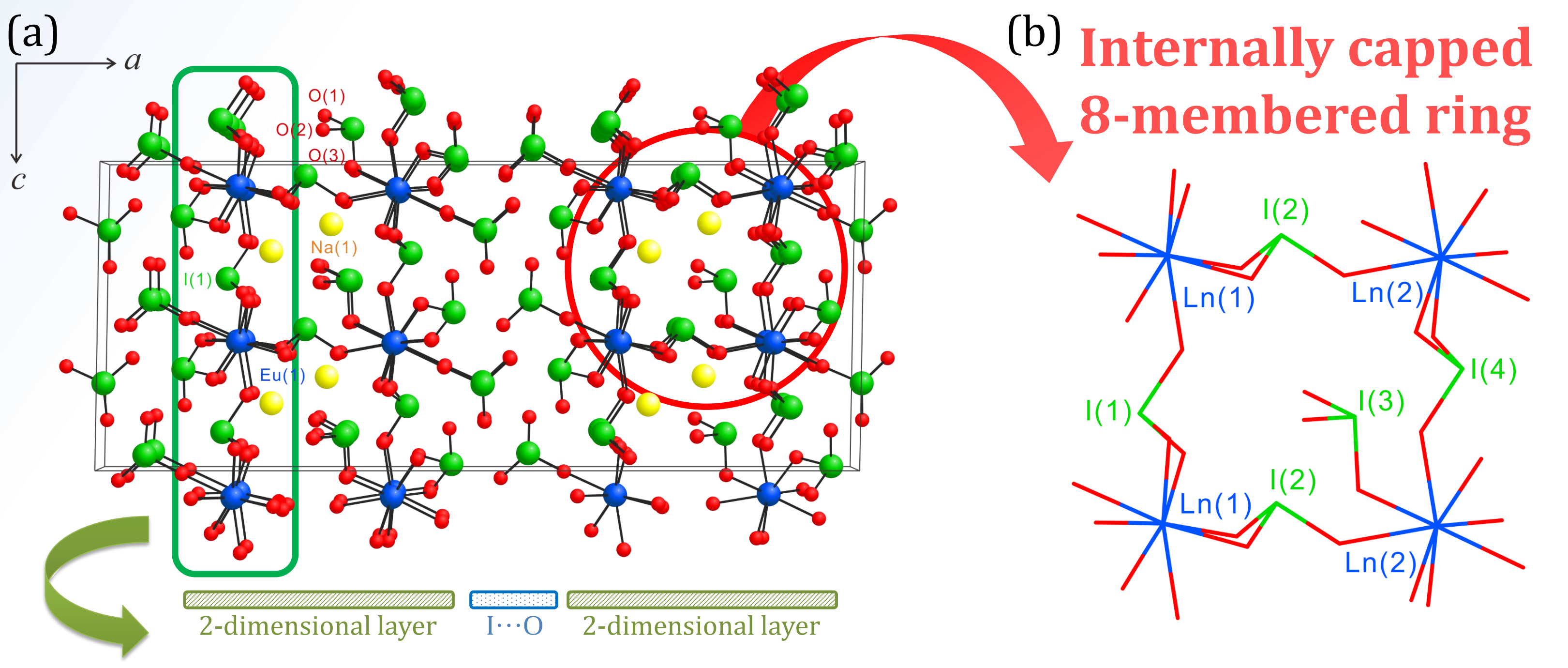
❖ Hydrothermal Reaction

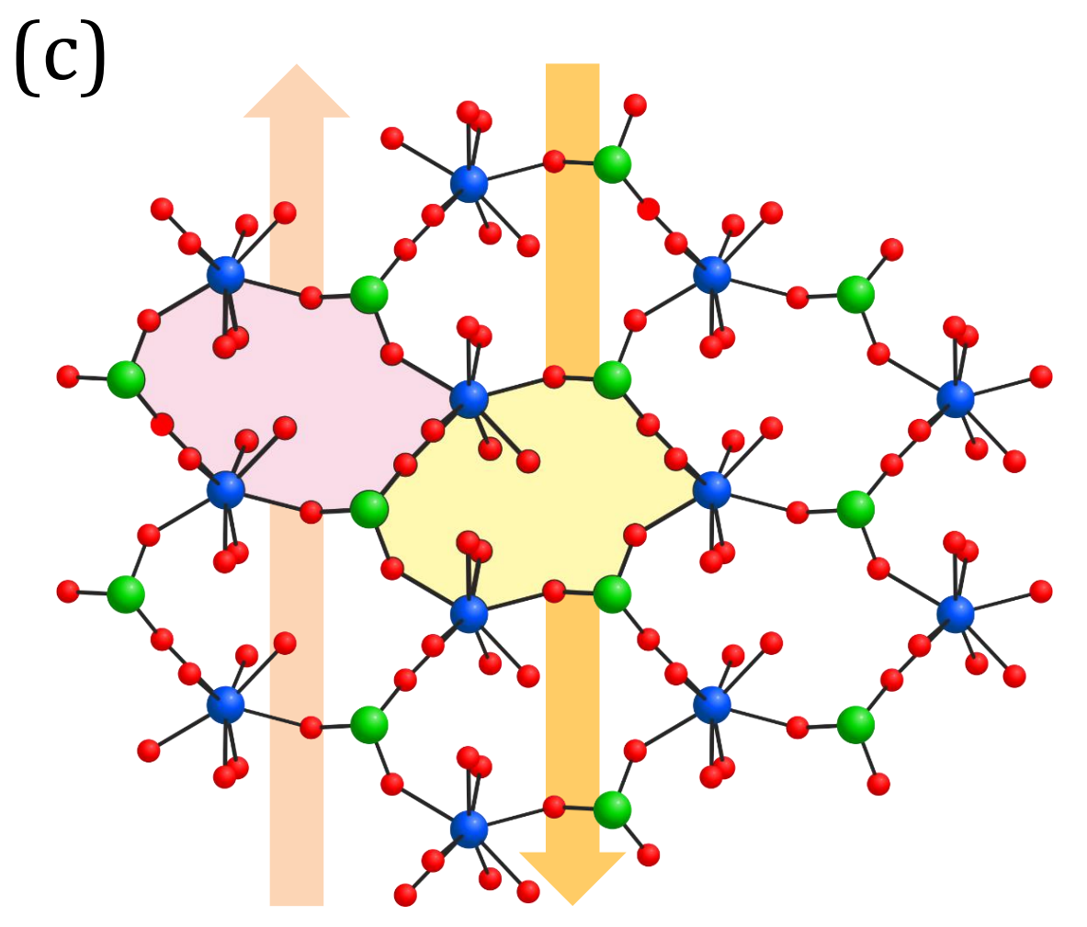
$$\text{excess } NaIO_3 + Ln(NO_3)_3 \cdot 6H_2O + HNO_3{}^{a} \xrightarrow[\Delta]{} NaLn(IO_3)_4, (Ln = La, Ce, Sm, \text{and } Eu)$$

[a] mineralizer



Crystal structure





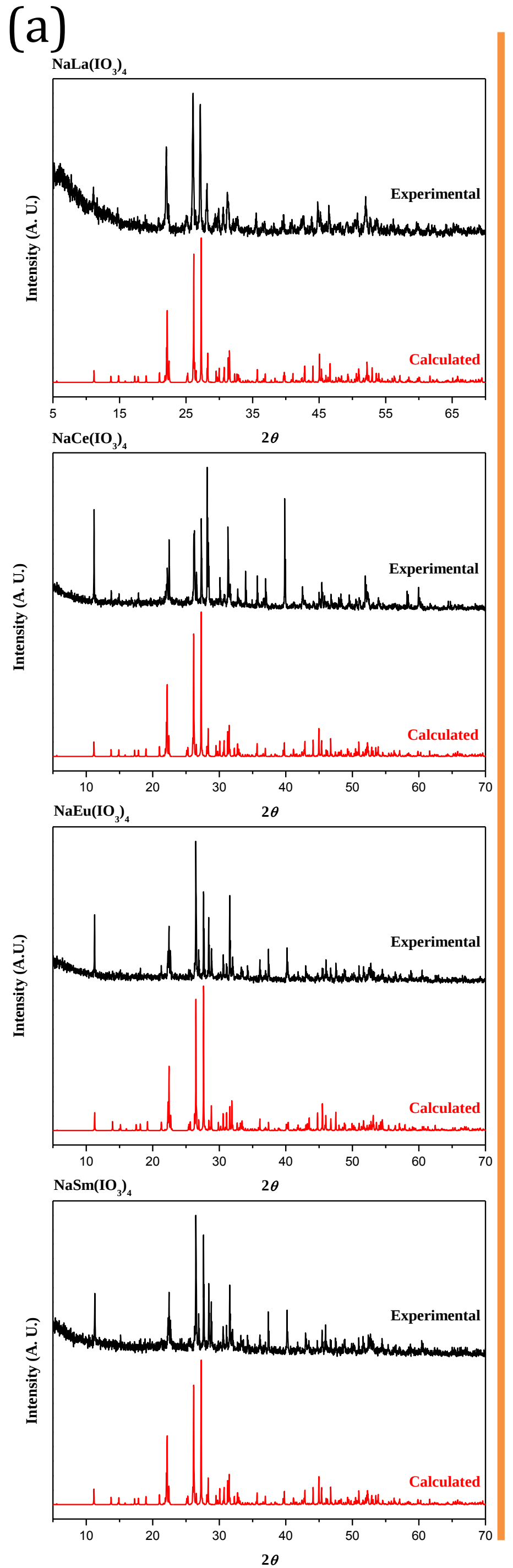
(a) Ball-and –stick representation of $NaLn(IO_3)_4$ crystal structure projected along the [010] direction.

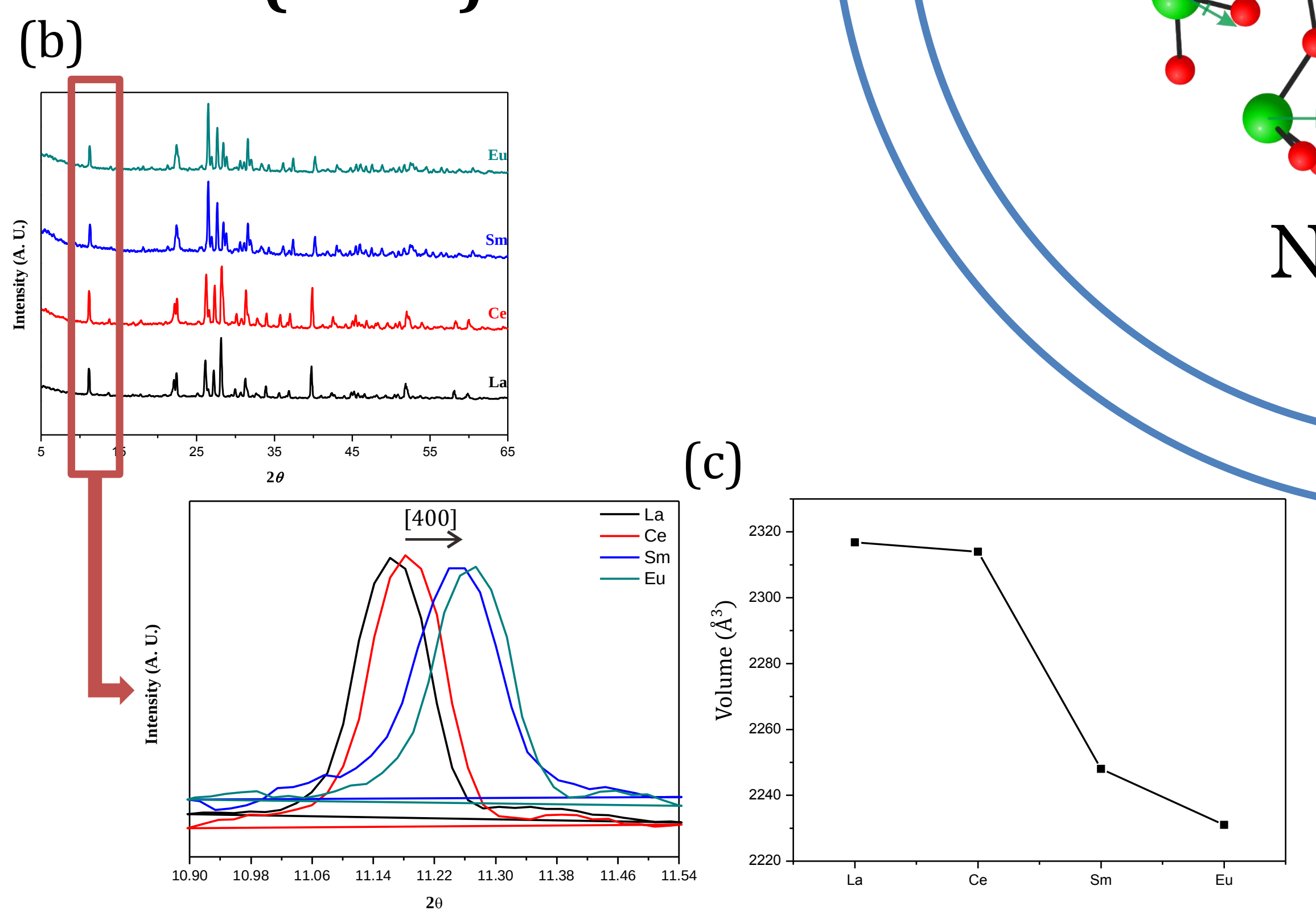
(b) Internally capped 8-membered ring channels are formed from four LnO_8 square-antiprisms and five IO_3 groups.

(c) Morphology of surface of the layer composed by 6-membered rings with two different direction.

Crystal-size distribution

Powder X-ray Diffraction (PXRD)



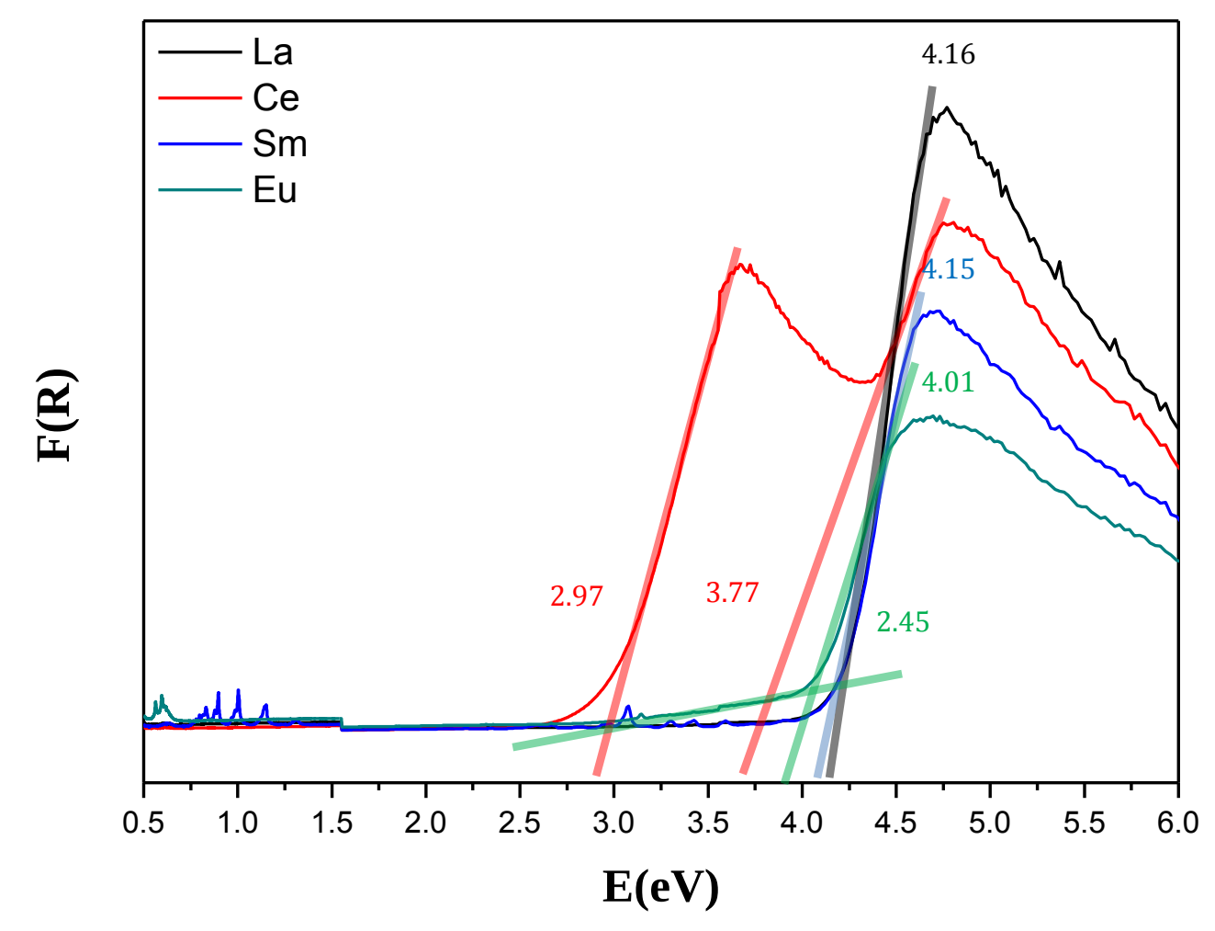


Formula	$NaLa(IO_3)_4$	$NaCe(IO_3)_4$	$NaSm(IO_3)_4$	$NaEu(IO_3)_4$
Formula weight (g mol^{-1})	861.52	862.72	872.96	874.57
Space group	*Cc* (No. 9)	*Cc* (No. 9)	*Cc* (No. 9)	*Cc* (No. 9)
a (Å)	31.656(6)	31.677(6)	31.4748(12)	31.3764(3)
b (Å)	5.6710(11)	5.6788(2)	5.6225(2)	5.6082(4)
c (Å)	12.906(3)	12.8794(5)	12.7071(4)	12.6829(10)
β (deg)	90.54(3)	90.74(8)	90.93(2)	90.98(3)
V (Å^3)	2316.8(8)	2314.58(17)	2248.44(2)	2231.42(4)
R(F)	0.0329	0.0295	0.0418	0.0470
$R_w(F_o)$	0.0778	0.0565	0.0819	0.1243

(a) The experimental and simulated PXRD pattern for each compounds. (b) Peak shift according to decrease of size of the cell. (c) decrease in the volume of the cell.

Characterization

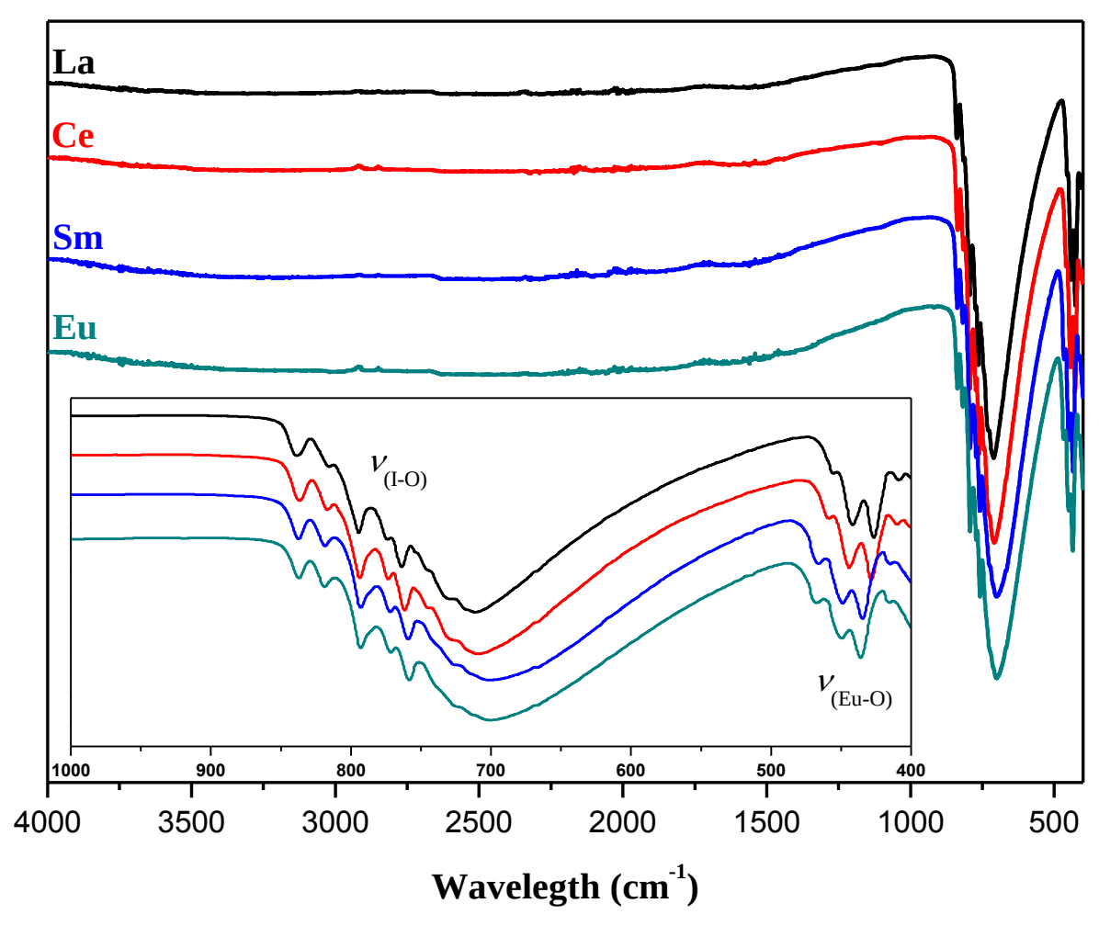
UV-Vis diffuse spectra



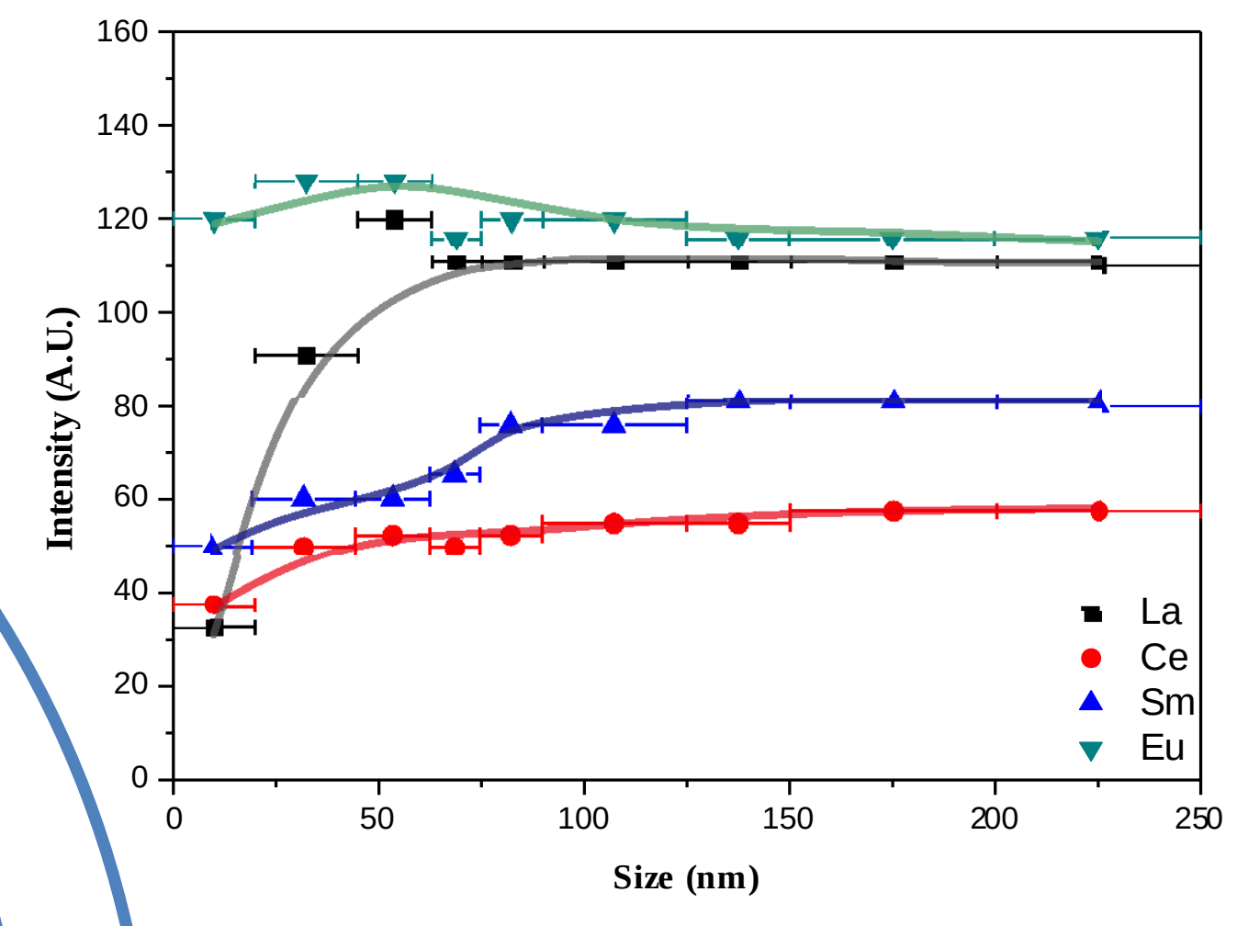
- The band gaps for the compounds $NaLn(IO_3)_4$ are calculated by using the Kubelka-Munk function and the compounds are insulators with band gaps of 2.97-4.16 eV.
- $NaCe(IO_3)_4$ and $NaEu(IO_3)_4$ shows absorption at ca. 417 nm (2.97 eV) and 504 nm (2.45 eV) that reveals yellowish and reddish colors, respectively.

IR spectra

- The IR spectra of all the compounds indicate that they are transparent in the range of mid-IR region (5-10 μm).
- The IR absorption bands at 600-850 cm^{-1} are due to the I-O vibrations, whereas those at 400-500 cm^{-1} are assigned to the Ln-O vibrations.



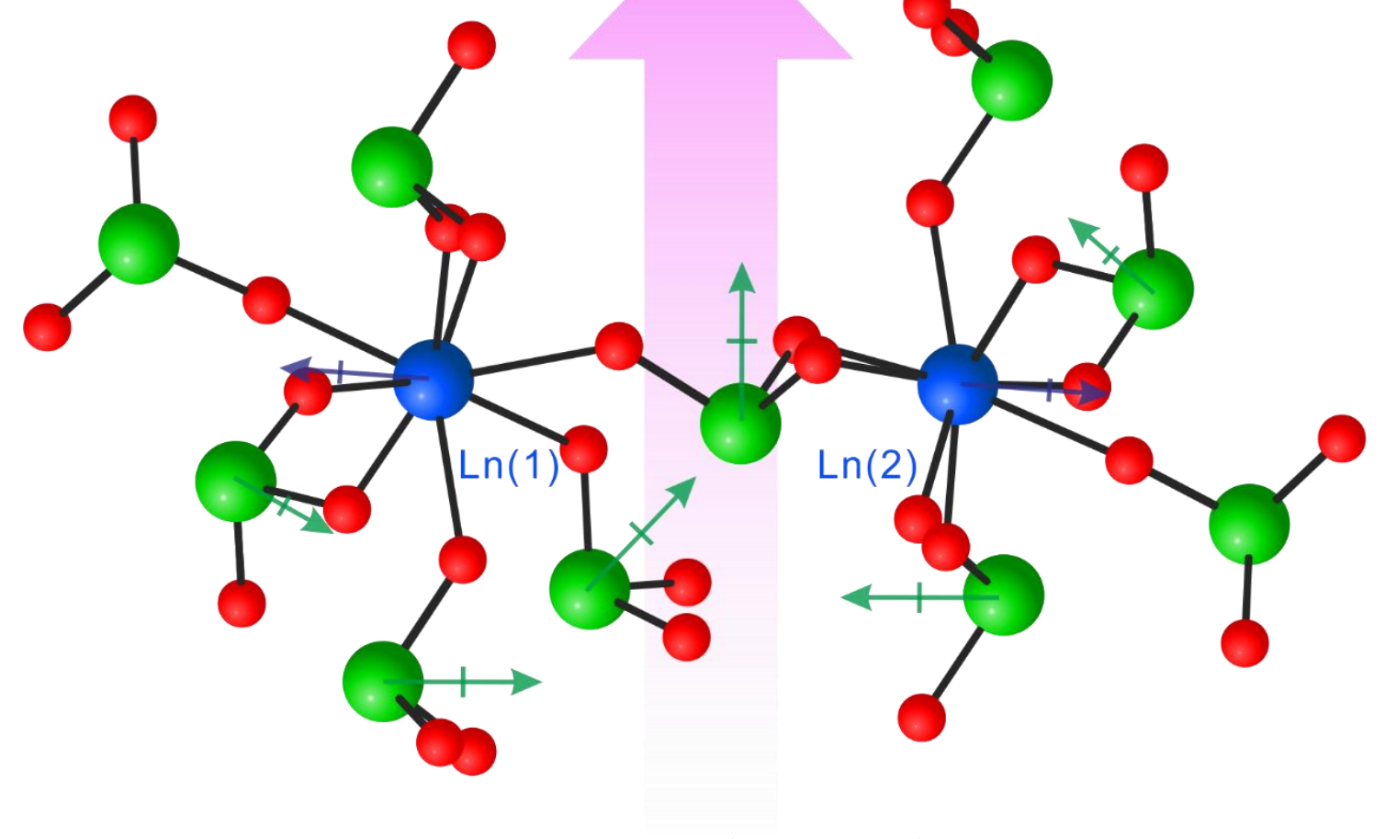
Second Harmonic Generation



Compound	SHG efficiencies (× α-SiO_2)
$NaLa(IO_3)_4$	100
$NaCe(IO_3)_4$	50
$NaSm(IO_3)_4$	80
$NaEu(IO_3)_4$	110

- The compounds reveal type-1 phase matching behavior and large SHG efficiencies

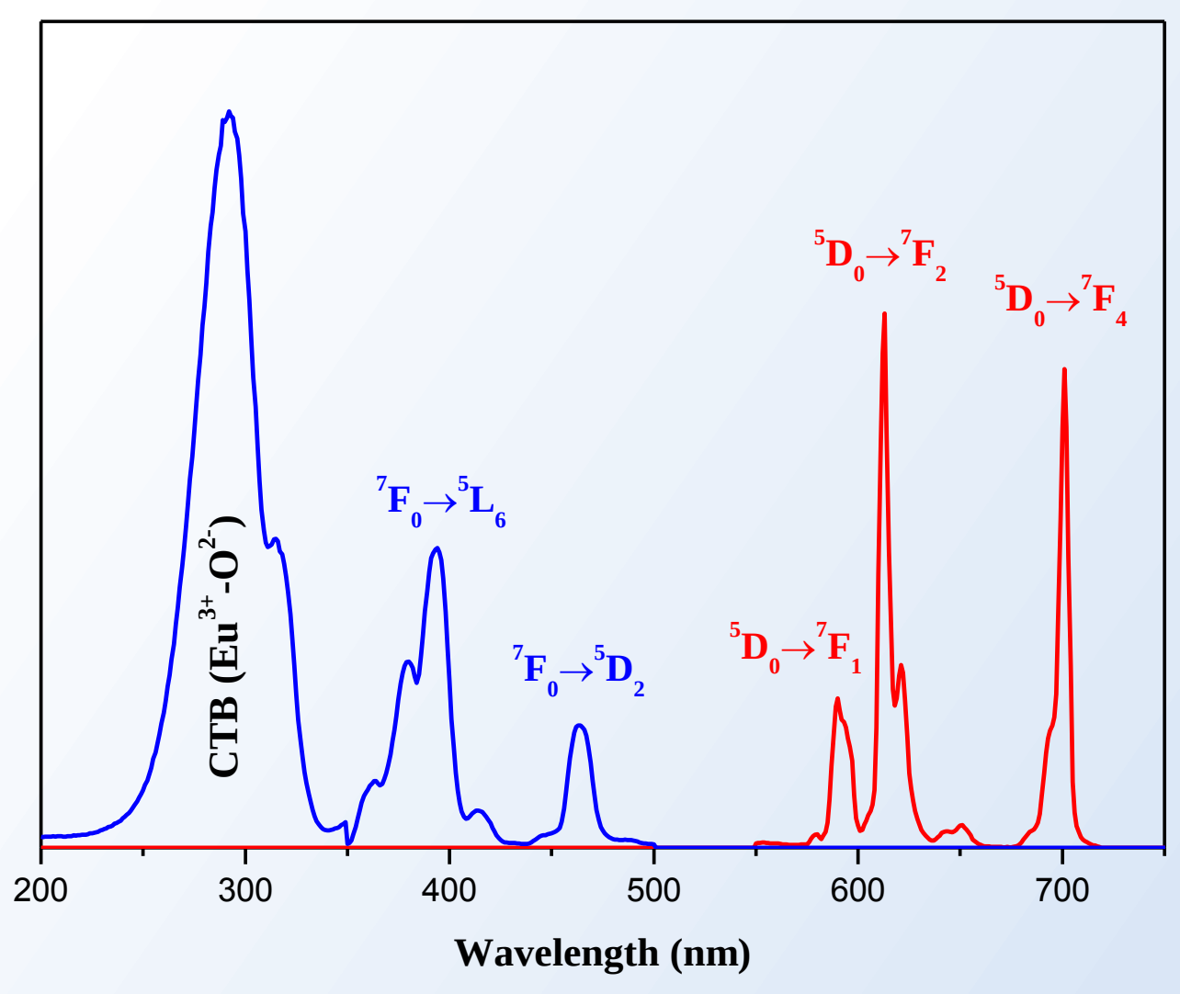
Asymmetric units



$NaLn(IO_3)_4$

PhotoLuminescence

- Excitation spectra (blue) and emission spectra (red) of $NaEu(IO_3)_4$ under 397 nm excitation and 597 nm emission, respectively.
- The electric dipole-allowed emission of $^5D_0 \rightarrow {}^7F_2$ is much powerful than magnetic dipole-allowed emission of $^5D_0 \rightarrow {}^7F_1$, which indicates that Eu^{3+} cations are under asymmetric environment.



Conclusion

A series of sodium lanthanide iodates, $NaLn(IO_3)_4$ (Ln=La, Ce, Sm, and Eu) have been successfully synthesized through hydrothermal reactions. The crystal structures are determined by SCXRD and confirmed by PXRD. The compounds reveal interesting optical properties related to the acentric crystal structures. The powder SHG measurements indicates that the materials reveal high SHG efficiencies with type-1 phase matching behavior. The PL properties suggest that the sites of Ln^{3+} cations are in asymmetric environment. The compounds are transparent up to 10 μm in IR region that may lead the materials use as source of laser for the mid-IR.

Acknowledgements: This work was supported by the Chung-Ang University Graduate Research Scholarship in 2016.