Photoluminescence Properties of Sm^{3+}- and Eu^{3+}-doped Noncentrosymmetric Iodates, $NaLa_{1-x}Ln_x(IO_3)_4$ (Ln = Sm and Eu)

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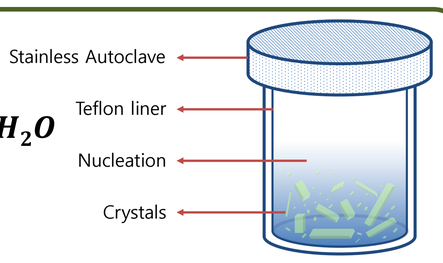
Abstract

Noncentrosymmetric (NCS) metal iodates are widely studied owing to their interesting properties, such as nonlinear optical (NLO), piezoelectric, pyroelectric, and ferroelectric properties. In particular, metal iodates containing cations with asymmetric coordination environments can exhibit interesting characteristics in photoluminescence (PL) properties. We synthesized a series of NCS iodate solid solutions, $NaLa_{1-x}Ln_x(IO_3)_4$ (Ln = Sm and Eu; x = 0, 0.05, 0.10, and 1) by hydrothermal reaction methods. The existence of the lanthanide cations are confirmed by the energy dispersive analysis by X-ray (EDX) with scanning electron microscopy (SEM). The structures for $NaLa_{1-x}Ln_x(IO_3)_4$ (Ln = Sm and Eu; x = 0 and 1) were determined by single crystal X-ray diffraction, whereas those of the doped materials were analyzed by powder X-ray diffraction using Rietveld method. $NaLa_{1-x}Ln_x(IO_3)_4$ exhibit layered structures composed of lanthanide cations and iodates, in which each layer is connected by I···O interactions. The oxygen atoms from IO_3^- iodate groups are coordinated to both lanthanide cations in distorted LnO_8 polyhedra. Powder second-harmonic generation (SHG) and photoluminescence properties of the materials are also reported.

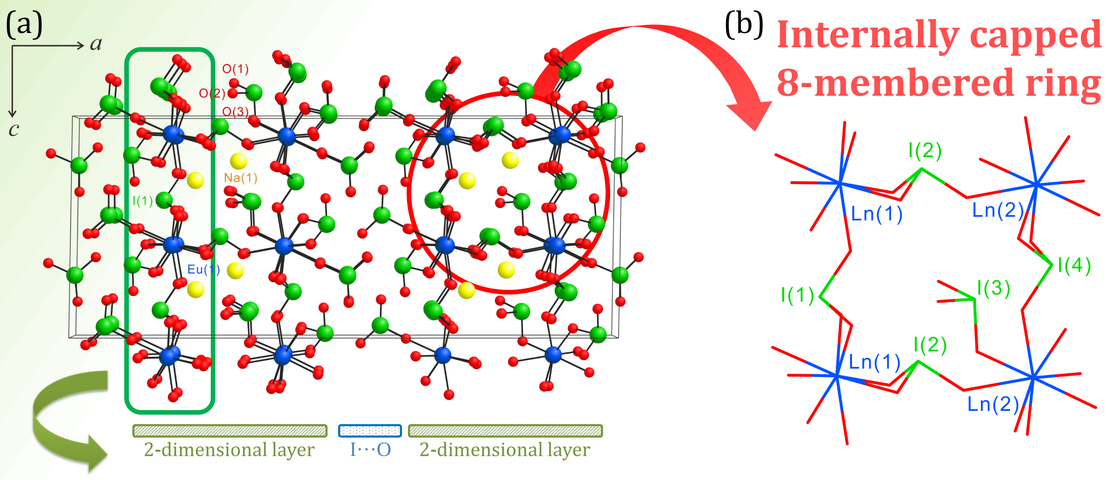
Synthesis

❖ Hydrothermal Reaction

$$NaIO_3 + (1-x)La(NO_3)_3 \cdot 6H_2O + xLn(NO_3) \cdot 6H_2O \xrightarrow[\Delta]{} NaLa_{1-x}Ln_x(IO_3)_4, (Ln = Sm, and\ Eu)$$



Crystal structure



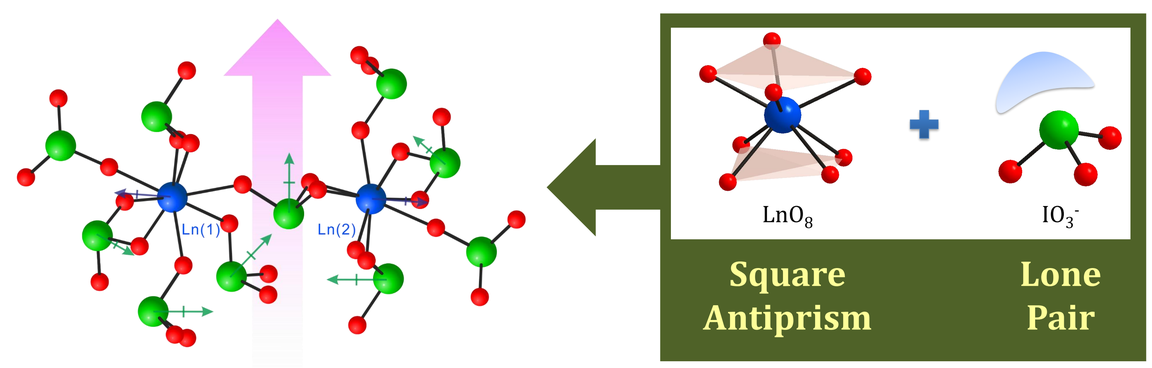
(a) Ball-and-stick representation of $NaLn(IO_3)_4$ crystal structure projected along the [010] direction.

(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.

Asymmetric Unit

❖ Asymmetric unit of $NaLn(IO_3)_4$



- The compounds contain asymmetric polyhedra, LnO_8 and IO_3 groups.
- Distortion of LnO_8 polyhedra is negligible compared to IO_3 groups.
- The net dipole moment from IO_3 groups toward to the *c*-direction is responsible for the large SHG efficiencies of the materials.

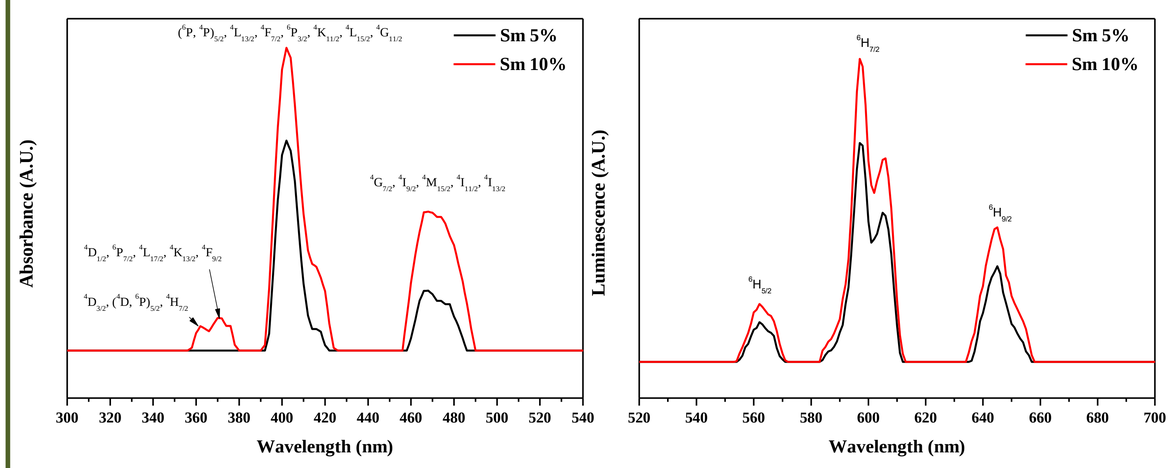
Calculation of Dipole Moments

Compounds	Species	Dipole moment (D)
$NaLa(IO_3)_4$	IO_3	13.8-16.6
	LaO_8	0.9-1.6
$NaSm(IO_3)_4$	IO_3	12.9-16.5
	SmO_8	0.9-1.8
$NaEu(IO_3)_4$	IO_3	13.5-16.3
	EuO_8	1.1-1.8

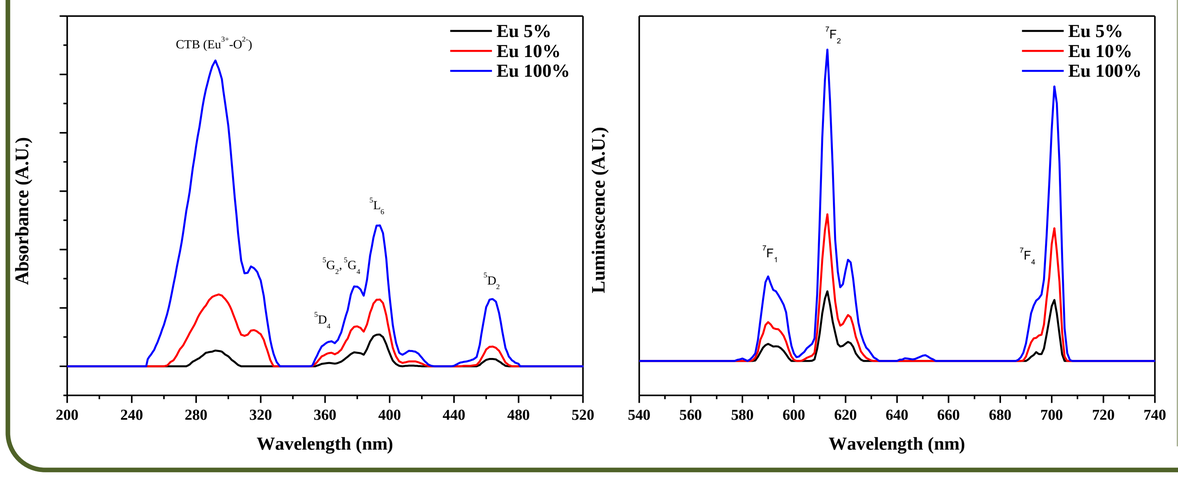
D = debyes

Optical Characterization

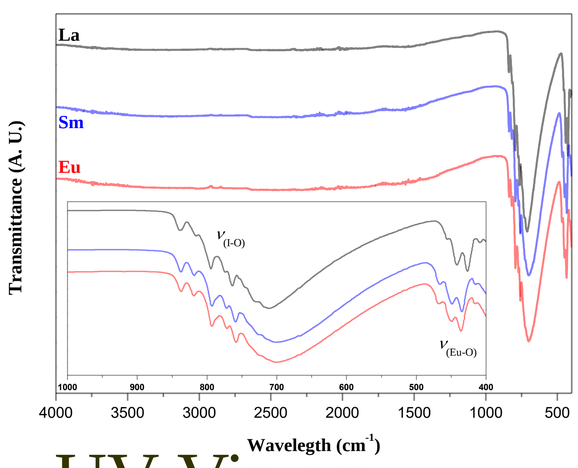
Photo-Luminescence



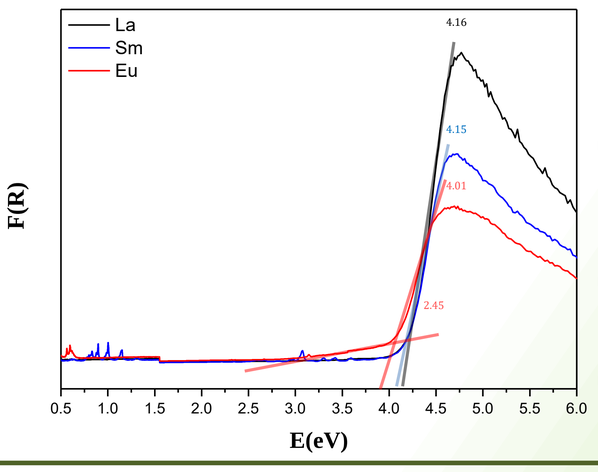
- Absorption from $^6H_{5/2}$ (Sm) and $^7F_0$ (Eu).
- Emission from $^4G_{5/2}$ (Sm) and $^5D_0$ (Eu).



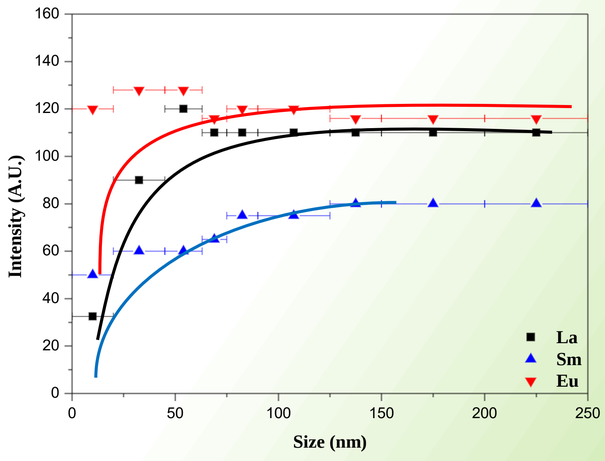
IR spectra



UV-Vis diffuse spectra



Second Harmonic Generation



- 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.
- $NaSm(IO_3)_4$ does not reveal PL properties attributed to the quenching effect with regard to concentration.
- The compounds are transparent in mid IR region.
- The reported materials are phase-matchable (type I) and reveal large SHG efficiencies.

Conclusion

A series of sodium lanthanide iodates, $NaLa_{1-x}Ln_x(IO_3)_4$ (Ln=La, 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 indicate 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 and Sm^{3+} doped compounds may reveal quenching effect depend on the doped-concentration. 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.

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