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Supporting Information

LiMg(IO₃)₃: An excellent SHG material designed by single-site aliovalent substitution

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Section S1 Materials and Methods

1. Syntheses.

LiCl (>99%), MgCl₂ (>98%), HCl (36–38%) and I₂O₅ (98%), were used as purchased from Adamas-beta. A mixture of starting materials of LiCl (6 mmol), MgCl₂ (1 mmol), I₂O₅ (2 mmol), and 3% HCl solution (2 mL) was put into Teflon pouches (23 mL) sealed in an autoclave which were heated at 230 °C for 72 hours, and cooled to the room temperature at 2 °C/h. Colorless prismatic crystals of LiMg(IO₃)₃ were isolated in yields of ~85% (based on Mg).

Instruments and Methods.

Powder X-ray Diffraction.

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku MiniFlex II diffractometer with graphite-monochromated Cu K α radiation in the 2 θ range of 10-70°.

Energy-dispersive X-ray spectroscope.

Microprobe elemental analyses were measured on a field-emission scanning electron microscope (FESEM, JSM6700F) equipped with an energy-dispersive X-ray spectroscope (EDS, Oxford INCA).

Thermal Analyses.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed with a NETZCH STA 449F3 unit under a N_2 atmosphere in the temperature range of 30-1000 °C, at a heating rate of 15 °C/min.

Optical Properties Measurements

S3

Infrared (IR) spectra were recorded on a Magna 750 FT-IR spectrometer in the form of KBr pellets in the range from 4000 to 400 cm^{-1} .

Ultraviolet-visible-near infrared (UV-vis-NIR) spectra in the range of 200-2400 nm were recorded on a PerkinElmer Lambda 950 UV-vis-NIR spectrophotometer.

Second Harmonic Generation Measurement.

Powder SHG measurements were performed on a Q switch Nd: YAG laser generating radiation at 1064 nm and 2.05 μ m based on the method of Kurtz and Perry.¹ Crystalline samples in the particle-size range of 150 - 210 μ m were used for SHG measurements. To test its phase matching ability, crystalline LMIO samples were sieved into distinct particle-size ranges (45 - 53, 53 - 75, 75 - 105, 105 - 150, 150 - 210, and 210 - 300 μ m). Sieved KH₂PO₄ (KDP) and KTP (KTiOPO₄) samples in the same particle-size ranges were used as references.

2. Single Crystal Structure Determination.

Single-crystal X-ray diffraction data was collected on an Agilent Technologies SuperNova dual-wavelength CCD diffractometer with Mo K α radiation ($\lambda = 0.71073$ Å) at 293 K. Data reduction was performed with the program *CrysAlisPro*, and absorption correction was applied as the multi-scan method.² The structure was solved by direct method and refined by full-matrix least-squares fitting on *F*² using *SHELXL– 2014*.³ All of the non-hydrogen atoms were refined with anisotropic thermal parameters. The structure was checked for missing symmetry elements using *PLATON* and none was found.⁴ The Flack factor was refined to 0.00(3), indicating that correctness of its absolute structures. A summary of crystallographic data and structure refinements are listed in Table S1. Selected bond distances are given in Table S2.

3. Laser Induced Damage Threshold Measurement.

LDT measurements were performed on crystalline sample of LMIO in the particlesize range of 150 - 210 μ m with the AgGaS₂ (AGS) sample in the same particle-size range as the reference, under a 1064 nm laser source (10 ns, 1 Hz). The area of the laser spot focused on the sample is 3.14 mm² for LMIO and AGS. The laser emission energy was gradually increased until the samples turned black in color. Notably, the LDT measurement using powder samples is feasible because each crystallite has a diameter much larger than the wavelength of the incident laser. Thus, each crystallite behaves as a macroscopic bulk material with similar multiphoton absorption (a main process for LDT as the laser pulse width is <50 ps).⁵

The SHG and LDT data of $Li_2M^{\mathbb{N}}(IO_3)_6$ ($M^{\mathbb{N}} = Ti$, Sn, and Ge) and α -LiIO₃ with the KDP and AGS as references were collected from ref. 6 under same experiment conditions.

4. Computational Method.

Single-crystal structural data of LMIO was used for the theoretical calculations. The electronic structures and optical properties were performed using a plane-wave pseudopotentials method within density functional theory (DFT) implemented in the total energy code CASTEP.⁷⁻⁸ For the exchange and correlation functional, Perdew-Burke-Ernzerhof (PBE) in the generalized gradient approximation (GGA) was applied.⁹ The interactions between the ionic cores and the electrons were described by the normconserving pseudopotential.¹⁰ The following valence-electron configurations were considered in the computation: Li 2s¹, Mg 2s²2p⁶3s², I 5s²5p⁵, and O 2s²2p⁴. The numbers of plane waves included in the basis sets were determined by cutoff energies of 900 eV. Monkhorst-Pack k-point sampling of $3 \times 3 \times 6$ was used to perform numerical integration of the Brillouin zone. During the optical property calculations, more than 170 empty bands were involved to ensure the convergence of linear optical property and SHG coefficient. The calculation of second-order NLO coefficient was based on length-gauge formalism within the independent-particle approximation. We adopted Sipe's formula, which had been described in details as (3.54), (3.55) and (3.56) in ref. 11. The first-order hyperpolarizability of M(IO₃)₆ clusters were calculated employing density functional theory (DFT) method implemented in Gaussian 09 program package at LanL2DZ level.¹²

formula	LiMg(IO ₃) ₃	
formula weight	555.95	
crystal system	hexagonal	
space group	<i>P</i> 6 ₃	
Т (К)	293(2)	
<i>a</i> (Å)	9.4139(10)	
<i>c</i> (Å)	5.1807(10)	
V (Å ³)	397.61(10)	
Ζ	1	
$D_{c} (g/cm^{-3})$	4.644	
μ (mm ⁻¹)	11.896	
GOF on F^2	1.108	
Flack factor	0.00(3)	
$R_1, wR_2 [I > 2\sigma(I)]^a$	0.0127, 0.0298	
R_1 , wR_2 (all data) ^a	0.0133, 0.0301	

 Table S1. Summary of Crystal Data and Structure Refinements for LMIO.

 ${}^{a}R_{1} = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|$, and $wR_{2} = \{\sum w[(F_{o})^{2} - (Fc)^{2}]^{2} / \sum w[(F_{o})^{2}]^{2}\}^{1/2}$.

Li(1)-O(1)	2.075(6)	Mg(1)-O(2)#4	2.076(2)
Li(1)-O(1)#1	2.075(6)	Mg(1)-O(2)#6	2.076(2)
Li(1)-O(1)#2	2.075(6)	Mg(1)-O(2)#7	2.076(2)
Li(1)-O(1)#3	2.088(5)	Mg(1)-O(3)	2.111(2)
Li(1)-O(1)#4	2.088(5)	Mg(1)-O(3)#8	2.111(2)
Li(1)-O(1)#5	2.088(5)	Mg(1)-O(3)#9	2.111(2)
I(1)-O(1)	1.7966(19)	I(1)-O(2)	1.815(2)
I(1)-O(3)	1.809(2)		

 Table S2. Selected bond distances (Å) for LMIO.

Symmetry transformations used to generate equivalent atoms:

#1 -y, x-y, z; #2 -x+y, -x, z; #3 y, -x+y, z+1/2; #4 -x, -y, z+1/2; #5 x-y, x, z+1/2; #6 -x-1, -y, z+1/2; #7 -y, x-y+1, z; #8 -x+y-1, -x, z; #9 -x+y-1, -x, z.

Table S3. Bond strain index (BSI), and Global instability index (GII) for LMIO and $Li_2M^{IV}(IO_3)_6$ (M =Ti, Sn, Ge).

	BSI	GII
Li ₂ Ti(IO ₃) ₆	0.108	0.431
Li ₂ Sn(IO ₃) ₆	0.051	0.312
Li ₂ Ge(IO ₃) ₆	0.130	0.194
LMIO	0.030	0.079



Figure S1. Simulated and measured powder X-ray diffraction patterns of LMIO.



Figure S2. The EDS spectrum of LMIO.



Figure S3. IR spectrum of LMIO.



Figure S4. The calculated band structure of LMIO.



Figure S5. The calculated refractive indices for LMIO.

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