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

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An excellent second harmonic generation (SHG) material, LiMg(IO₃)₃ (LMIO), has been elaborately designed from Li₂MIV(IO₃)₆ (MIV = Ti, Sn, and Ge) by aliovalent substitution of the central MIV cation followed by Wyckoff position exchange. The new structure sustains the ideal-alignment of (IO₃)⁻ groups. Importantly, LMIO exhibits an extremely strong SHG effect of roughly 24 × KDP under 1064 nm laser radiation or 1.5 × AgGaS₂ (AGS) under 2.05 μm laser radiation, which is larger than that of α-LiIO₃ (18 × KDP). The replacement of MIV with Mg²⁺ without d–d electronic transitions induces an obviously larger band gap (4.34 eV) with a short absorption edge (285 nm). This study shows that single-site aliovalent substitution provides a new synthetic route for designing SHG materials.

**Introduction**

Noncentrosymmetric (NCS) or polar crystals have attracted scientific endeavors since they are potential candidates as SHG materials.1–13 Metal iodates with polar units, (IO₃)⁻ or IO₃⁻, are a class of important compounds which can exhibit excellent SHG performance.5 Numerous synthetic efforts have been made and afforded a number of iodates with outstanding SHG properties,1,4 such as BiO(IO₃) (12.5 × KDP)6 and Gd₂IO₁₄ (15 × KDP).7 However, generally, the larger SHG effects of iodates are usually accompanied by smaller band gaps. Recently, aliovalent substitution has become an effective approach for exploring novel SHG crystals.5,9,11 Aliovalent substitution of BiO(IO₃) gave BiFSeO₃, which has the highest SHG effect among selenites reported.9 The novel route of aliovalent substitution involving three atom sites has expended d⁰-TM cations to post main group cations, such as from V⁵⁺ to Ga³⁺.10 In this way, isotopic compounds sustained both large polarizability and a wide band gap.10 For example, α- and β-Ba₂[GaF₄(IO₃)₂] (6 × KDP; 4.61 and 4.31 eV)11 have clearly larger band gaps and slightly weaker SHG signals than α- and β-Ba₂[VO₂F₄(IO₃)₂] (9 × KDP; 2.59 and 2.55 eV).11

Recently, a serial of isostructural SHG iodates, namely Li₅MIV(IO₃)₆ (MIV = Ti, Sn, and Ge), were reported, whose structures feature well-arranged (IO₃⁻) units. The regulation of Ti⁴⁺, Sn⁴⁺ and Ge⁴⁺ cations induces SHG effects shifting from 17 ×, 15 ×, to 32 × KDP and band gaps changing from 3.0, 3.9 to 3.89 eV for Ti, Sn and Ge compounds, respectively.11 Interestingly, in these structures, both Li⁺ and M⁴⁺ cations are octahedrally coordinated but they occupy different Wyckoff positions. The Li⁺ cation site on 2b and the LiO₆ octahedra are bridged by iodate groups into a 3D [Li₂[IO₃]₂]⁺ framework. M⁴⁺ cations located at 2a are only 50% occupied and 0D [MIV(IO₃)₆]³⁻ polyanions were formed. The full occupation of MIV would be not consistent with the colorless and insulating crystals, which had been discussed in detail by P. Shiv Halasyamani.11,12 We consider that aliovalent substitution of the M⁴⁺ cation with two divalent metal ions may result in LiMII(IO₃)₃ with a completely ordered structure, and this expands the family of this class of metal iodates with excellent SHG effects. Additionally, the use of alkaline-earth cations can avoid the unfavorable d–d electronic transitions for the transition metal ions and favors the blue-shift of the absorption edge. By using such a single-site aliovalent substitution method, LiMg(IO₃)₃ (LMIO) was designed from Li₅MIV(IO₃)₆ via replacing the defect-containing M⁴⁺ cation with an ordered Mg³⁺ cation followed by Wyckoff position exchange. In LMIO, a 3D [Mg(IO₃)₆]³⁻ anionic framework is formed instead of 0D [MIV(IO₃)₆]³⁻ anions. LMIO displays an extremely large SHG response (24 × KDP under 1064 nm laser radiation or 1.5 × AGS under 2.05 μm laser radiation), large band gap (4.34 eV), high LDT (46 × AGS) and good thermal stability (>500 °C).

**Results and discussion**

Polar LMIO was prepared by hydrothermal reactions of LiCl, MgCl₂, I₂O₅ and 3% HCl solution at 230 °C for 3 days. Its purity

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was checked by PXRD study and EDS elemental analyses (Fig. S1 and S2†).

LMIO crystallizes in the NCS and polar space group P63 (no. 173). The asymmetric unit of LMIO contains one Li, one Mg, one I, and three O atoms. Both Li and Mg atoms occupy sites with 3-fold axis symmetry whereas the remaining atoms are located at the normal sites. Both Li\(^+\) and Mg\(^{2+}\) cations connect with six O atoms to form LiO\(_6\) and MgO\(_6\) octahedra, and each octahedron links with six (IO\(_3\))\(^-\) groups which are ideally aligned along the \(c\) direction, leading to very large polarizability.

The lengths of the Li–O bond (2.075(6) and 2.088(5) \(\AA\)) and Mg–O bond (2.076(2) and 2.111(2) \(\AA\)) are pretty close indicating that the distortions of LiO\(_6\) and MgO\(_6\) are very small. The I\(^5+\) atom is three coordinated in a triangular-pyramidal geometry with I–O bond lengths of 1.7966(19), 1.809(2) and 1.815(2) \(\AA\). BVS calculations exhibit the values of 1.14 (Li), 2.03 (Mg) and 5.06 (I), verifying that these cations are in oxidation states of +1, +2 and +5, respectively.

Neighboring LiO\(_6\) octahedra are inter-linked into a 1D chain along the \(c\)-axis via face-sharing (Fig. 1a) whereas neighboring MgO\(_6\) octahedra are bridged by iodate groups into a 3D [Mg(IO\(_3\))\(_6\)]\(^{4-}\) anionic framework with 1D tunnels of Mg\(_6\)I\(_6\) 12-membered rings (MRS) (Fig. 1b). The overall structure of LMIO can be viewed as the 1D chains of face-sharing LiO\(_6\) octahedra inserted into the 1D tunnels of the 3D [Mg(IO\(_3\))\(_6\)]\(^{4-}\) anionic framework (Fig. 1c). Because that a process of Wyckoff position exchange occurred as the structural evolution from Li\(_2\)MIV(IO\(_3\))\(_6\) to LMIO and different occupancy of the cation at the 2a position (fully occupied Li\(^+\) in LMIO but 50% occupied M\(^{4+}\) in Li\(_2\)MIV(IO\(_3\))\(_6\)), it is interesting to note that there is in the structures of Li\(_2\)MIV(IO\(_3\))\(_6\) (M = Ti, Sn, Ge), neighboring LiO\(_6\) octahedra or [MIV(IO\(_3\))\(_6\)]\(^{2-}\) anions are not interconnected, that is they are isolated.\(^{11}\)

The ionic radii of the six-coordinated Li\(^+,\)Mg\(^{2+},\)Ti\(^{4+},\)Sn\(^{4+},\) and Ge\(^{4+}\) are 0.076, 0.072, 0.0605, 0.069, and 0.053 nm, respectively.\(^{12}\)

Obviously, the ionic radius of Mg\(^{2+}\) is much closer to that of Li\(^+\) than that of M\(^{4+}\). Thus, Wyckoff position exchange occurred during the aliovalent substitution of M\(^{4+}\) with Mg\(^{2+}\) cations. In addition, our calculations of total energy show that LMIO (–12 816.63 eV) is more energy-favorable than the one adopting the Li\(_2\)MIV(IO\(_3\))\(_6\) structural type (–12 814.03 eV). Attempts to replace Li\(^+\) in LMIO with Na\(^+\) to get an isostructural sodium phase were not successful, probably owing to the much larger size of Na\(^+\) (0.102 nm). We consider that a disordered M\(^{3+}\) cation, such as Al\(^{3+}\) and Ga\(^{3+}\) with 67% occupancy, may replace the M\(^{4+}\) cation in Li\(_2\)MIV(IO\(_3\))\(_6\) (M = Ti, Sn, Ge).

The calculations of bond strain index (BSI) and global instability index (GII) values gave small values of 0.030 (BSI) and 0.079 (GII) for LMIO, which indicated that the structure of LMIO is unstrained and stable.\(^{13,14}\) The corresponding BSI and GII values of Li\(_2\)MIV(IO\(_3\))\(_6\) (M = Ti, Sn, Ge) are much larger than those of LMIO (Table S3†), which are consistent with the disorder in Li\(_2\)MIV(IO\(_3\))\(_6\) (M = Ti, Sn, Ge).

Thermogravimetric analysis (TGA) reveals the high thermal stability (>500 °C) of LMIO (Fig. 2). It shows two steps of weight loss in 500–650 °C (sharp) and 750–910 °C (smooth), and both are related to the release of I\(_2\) and O\(_2\). The DSC curves exhibit three endothermic peaks at 610, 647 and 903 °C and one exothermic peak at 626 °C. Compared to Li\(_2\)MIV(IO\(_3\))\(_6\) (M = Ti, Sn, Ge) (–400 °C), LMIO has higher thermal stability.\(^{11}\)

![Fig. 1 A 1D chain of face-sharing LiO\(_6\) octahedra along the c-axis (a); the 3D [Mg(IO\(_3\))\(_6\)]\(^{4-}\) anionic framework along the c-axis (b); and the view of the structure of LMIO along the c-axis (c).](image1)

![Fig. 2 TG and DSC analyses of LMIO.](image2)
The IR spectrum shows that LMIO is transparent in the wavelength region of 2.5–11.2 μm (4000–890 cm⁻¹) (Fig. S3†). The UV-Vis-IR study revealed the absorption edge of 285 nm for LMIO (Fig. 3). Hence, the transparent range (0.28–11.2 μm) of LMIO covers the UV, Visible and mid-IR regions. The band gap of LMIO (4.34 eV) is significantly wider than those of Li₂M̅(IO₃)₆ (M = Ti, Sn, Ge) (3.0, 3.9 and 3.86 eV for Ti, Sn and Ge compounds, respectively).¹¹

Powder SHG experiments indicate that LMIO is a phase-matchable SHG material with remarkable SHG signals of 24 × KDP under 1064 nm laser radiation or 1.5 × AGS under 2.05 μm laser radiation (Fig. 4). Compared with commercial α-LiIO₃ (18 × KDP), LMIO possesses an obviously enhanced SHG signal. The SHG response of LMIO is also much larger than those of Li₂Ti(IO₃)₆ (17 × KDP) and Li₂Sn(IO₃)₆ (15 × KDP) but is slightly smaller than that of Li₂Ge(IO₃)₆ (32 × KDP). Eliminating the influence induced by the disorder effect, we adopt the Gaussian09 program to calculate the first-order
hyperpolarizabilities of $[\text{Mg}(\text{IO}_3)_6]^{4-}$ and $[\text{M}^{IV}(\text{IO}_3)_6]^{2-}$ anions ($\text{M} = \text{Ti}, \text{Sn}$ and $\text{Ge}$), which are obtained to be 3047, 2982, 2602 and 1707 a.u. for Ge, Mg, Sn, and Ti, respectively, and such a trend is roughly consistent with results from the SHG measurements ($\text{Li}_2\text{Ge}(\text{IO}_3)_6 > \text{LMIO} > \text{Li}_2\text{Sn}(\text{IO}_3)_6 \approx \text{Li}_2\text{Ti}(\text{IO}_3)_6$). Notably, LMIO is the only NLO material featuring excellent optical nonlinearity ($>20 \times \text{KDP}$) and a near-UV absorption edge ($<300$ nm).

LDT experiments revealed a large value of 101.86 MW cm$^{-2}$ for LMIO, which is about 46 times that of AGS (2.22 MW cm$^{-2}$). This value is comparable to those of $\text{Li}_2\text{M}^{IV}(\text{IO}_3)_6$ ($\text{M} = \text{Ti}, \text{Sn}, \text{Ge}$) (49, 41, and 42 $\times$ AGS for Ti, Sn, and Ge compounds, respectively) and $\alpha$-$\text{LiIO}_3$ (54 $\times$ AGS)$^{14d}$

Theoretical calculations based on DFT methods were applied for understanding the source of the outstanding SHG effect. Band structure calculations revealed that LMIO is an indirect band gap compound with a gap of 3.35 eV (Fig. S4†), which is much smaller than the measured value (4.34 eV). Hence scissor of 0.99 eV was applied during the subsequent optical property analyses.

The partial density of states (PDOS) was studied for the energy band assignment and bond interaction (Fig. 5). In the whole energy region, full overlapping of the electronic states between I atoms and O atoms is observed, indicating strong interactions in I–O bonds. The band gap of LMIO is determined by IO$_3$ units because the nonbonding orbitals from I and O
Conflicts of interest
The authors declare no competing financial interest.

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Notes and references


