Hydrothermal Synthesis of new Mixed-Oxoanion Materials: Rare Earth Iodate Sulfates $Sm(IO_3)(SO_4)$ and $Ln_2(IO_3)_3(SO_4)OH•3H_2O$ (Ln = Sm, Eu, Dy)

Ceren Kutahyali Aslani[a], Vladislav V. Klepov[a], and Hans-Conrad zur Loye[*a]

[a]Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC
29208, USA

*corresponding author email: zurloye@mailbox.sc.edu

Abstract

Chemical systems that contain non-centrosymmetric anions with electron lone pairs promote the formation of non-centrosymmetric phases. To probe this approach in mixed anion systems, we investigated crystallization in iodate-sulfate systems under mild hydrothermal conditions. By using different SO_4 concentrations, the $Sm(IO_3)(SO_4)$ and $Ln_2(IO_3)_3(SO_4)OH{\bullet}3H_2O$ (Ln = Sm, Eu, Dy) structures were synthesized. It was observed that the reaction was very sensitive to the sulfate concentration. The structures were determined by single-crystal X-ray diffraction, where $Sm(IO_3)(SO_4)$ crystallizes in the monoclinic crystal system adopting the space group $P2_1/c$ and $Ln_2(IO_3)_3(SO_4)OH{\bullet}3H_2O$ (Ln = Sm, Eu, Dy) crystallize in the triclinic crystal system adopting the space group $P\overline{1}$.

Introduction

Numerous iodate compounds have been explored for their often noncentrosymmetric (NCS) structures, which can lead to useful non-linear optical (NLO) properties.[1–10] In fact, the search for improved NLO behavior has been the dominating driving forces behind most efforts to synthesize new iodate materials and has resulted in the synthesis of several hundred iodate compositions to date.[1–10] What makes iodates so interesting is that fact that iodates containing the I^{5+} species can take on two types of coordination environments, that of $[IO_3]^-$ and of $[IO_4]^{3-}$, where the lone pair on the I^{5+} species causes many iodate containing structures to crystallize in NCS structures. To expand upon the iodate chemistry, several groups have explored iodate sulfates, such as $Na_7(IO_3)(SO_4)_3$,[11] $Bi(IO_3)(SO_4)$,[12] $CdBi(IO_3)(SO_4)_2$[12] and $Ce(IO_3)_2(SO_4)$,[13] in their search for new NLO and other materials. It is a reasonable expectation that the combination of multiple anions into a single structure can lead to new structure types with, perhaps, improved physical properties. Sulfate chemistry has been studied for over 100 years and the tetrahedral SO_4 building block is readily accommodated by most cations, as evidenced by the fact that metal sulfates are known for essentially every known element. Thus, the sulfate group is an excellent choice of an anion for targeting mixed anion materials.

Our interest in multi anion systems was prompted by our past investigation of luminescing rare earth iodates, $Ln2(IO_3)_3(IO_4)$ (Ln=La, Nd, Pr) [14] where we encountered iodate sulfate products when using H_2SO_4 to adjust the pH in our iodate syntheses. We decided to pursue their targeted synthesis via hydrothermal synthesis and explored various reaction conditions to yield iodate sulfates rather than the simple iodates. Herein, we report reaction conditions optimization that led to the crystallization of $Sm(IO_3)(SO_4)$ and $Ln_2(IO_3)_3(SO_4)OH{\bullet}3H_2O$ (Ln = Sm, Eu, Dy) in centrosymmetric space groups. $Sm(IO_3)(SO_4)$ is isostructural with $Bi(IO_3)(SO_4)$,[12] $Ln(IO_3)(SO_4)$ (Ln = La–Gd, except Pm) [15] and $Ln(IO_3)(SeO_4)$ (Ln = La–Nd),[9] which all crystallize in the monoclinic space group $P2_1/c$, while $Ln_2(IO_3)_3(SO_4)OH{\bullet}3H_2O$ (Ln = Sm, Eu, Dy) represent new compositions and structures that crystallize in the triclinic space group $P\,\bar{1}$. We suggest that the synthetic routes developed, and described below, to obtain the mixed iodate sulfate polyanion materials can readily be extended to other systems, such as iodate phosphates, iodate arsenates, or iodate vanadates.

EXPERIMENTAL

Reagents

Sm_2O_3 (Alfa Aesar, 99.99%), Eu_2O_3 (Alfa Aesar, 99.99%), Dy_2O_3 (Alfa Aesar, 99.9%), HIO_3 (Alfa Aesar, 99%), H_2SO_4 (Fisher), Cs_2SO_4 (Alfa Aesar, 99.99%) were all used as received.

Synthesis

For $Sm(IO_3)(SO_4)$ (**1**), 0.349 g (1 mmol) of Sm_2O_3 and 0.528 g (3 mmol) of HIO_3 were combined with 4.5 mL of H_2O and 0.5 mL conc. H_2SO_4. For $Sm_2(IO_3)_3(SO_4)OH•3H_2O$ (**2**), 0.349 g (1 mmol) of Sm_2O_3 and 0.362 g (1 mmol) Cs_2SO_4 and 0.528 g (3 mmol) of HIO_3 were combined with 5 mL of H_2O. Another route that yields the same product, $Sm_2(IO_3)_3(SO_4)OH•3H_2O$, involves combining 0.349 g (1 mmol) of Sm_2O_3 and 0.528 g (3 mmol) of HIO_3 with 3 mL of H_2O and 2mL of 1N H_2SO_4. For $Eu_2(IO_3)_3(SO_4)OH•3H_2O$, (**3**) 0.352 g (1 mmol) of Eu_2O_3 and 0.362 g (1 mmol) Cs_2SO_4 and 0.528 g (3 mmol) of HIO_3 were combined with 5 mL of H_2O. For $Dy_2(IO_3)_3(SO_4)OH•3H_2O$, (**4**) 0.373 g (1 mmol) of Dy_2O_3 and 0.528 g (3 mmol) of HIO_3 were combined with 3 mL of H_2O and 2 mL of 1N H_2SO_4.

Each solution was placed in a 23-mL Teflon-lined autoclave that was subsequently sealed. The autoclaves were gradually heated to 220°C, held for 4 days, and cooled slowly to room temperature at a rate of 6°C h^{-1}. The products were recovered by filtration and washed with water. Colorless crystals of $Sm(IO_3)(SO_4)$, $Eu_2(IO_3)_3(SO_4)OH•3H_2O$ and $Dy_2(IO_3)_3(SO_4)OH•3H_2O$ and yellow crystals of $Sm_2(IO_3)_3(SO_4)OH•3H_2O$ were obtained in good yield.

Single Crystal X-ray Diffraction

Single-crystal X-ray diffraction data were collected at 300(2) K on a Bruker D8 QUEST diffractometer equipped with an Incoatec IμS 3.0 microfocus radiation source (M_oK_α, $\lambda = 0.71073$ Å) and a PHOTON II area detector. The crystals were mounted on a microloop using immersion oil. The raw data reduction and absorption corrections were performed using SAINT and SADABS programs. [16, 17] Initial structure solutions were obtained with SHELXS-2017 using direct methods and Olex2 GUI.[18] Full-matrix least-squares refinements against F^2 were performed with SHELXL software. [19] All atoms including hydrogen (except the hydrogen atoms of non-coordinated water molecules) were located in difference electron density map. The O–H bonds in H_2O and OH groups were restrained to 0.95 Å before final structure refinement. The crystallographic data and results of the diffraction experiments are summarized in Table 1.

Table 1. Crystallographic Data for $Sm(IO_3)(SO_4)$ and $Ln_2(IO_3)_3(SO_4)OH\bullet 3H_2O$, Ln: Sm, Eu, Dy

Chemical formula	$Sm(IO_3)(SO_4)$	$Sm_2(IO_3)_3(SO_4)OH\bullet 3H_2O$	$Eu_2(IO_3)_3(SO_4)OH\bullet 3H_2O$	$Dy_2(IO_3)_3(SO_4)OH\bullet 3H_2O$
Formula weight	421.31	992.52	993.72	1014.80
Crystal system	monoclinic	triclinic	Triclinic	triclinic
Space group, Z	$P\ 2_1/c$	$P\ \bar{1}$	$P\ \bar{1}$	$P\ \bar{1}$
a, Å	9.3148(9)	7.3858(2)	7.3666(2)	7.3088(2)
b, Å	6.8678(7)	9.6166(3)	9.5817(3)	9.4824(3)
c, Å	8.2852(8)	11.8629(3)	11.8263(3)	11.7302(3)
V, Å^3	512.67(9)	718.23(4)	711.85(3)	694.63(3)
ρ_{calcd}, g/cm^3	5.458	4.589	4.636	4.852
Radiation (λ, Å)	MoKα (0.71073)			
μ, mm^{-1}	17.859	14.780	15.474	17.586
T, K	303	302	302	302
Crystal dim., mm^3	0.05x0.05x0.02	0.07x0.07x0.07	0.07x0.07x0.07	0.07x0.07x0.03
2θ range, deg.	2.260- 36.319	2.967-27.495	3.113-28.494	2.526-29.998
Reflections collected	20573	36615	46001	51463
Data/parameters/restraints	2477/41/0	3294/209/0	3555/229/5	4038/229/5
R_{int}	0.0339	0.0340	0.0329	0.0334
Goodness of fit	1.200	1.085	1.027	1.079
$R_1(I > 2\sigma(I))$	0.0301	0.0152	0.0133	0.0131
wR_2(all data)	0.1323	0.0368	0.0315	0.0304

Powder X-ray Diffraction

Powder X-ray diffraction (PXRD) data were collected on polycrystalline samples ground from single crystals. Data were collected on a Bruker D2 PHASER diffractometer using Cu Kα radiation over a 2θ range 10−65° with a step size of 0.02°.

Energy-Dispersive Spectroscopy (EDS)

EDS was performed on single crystal products using a Tescan Vega-3 SEM equipped with a Thermo EDS attachment. The SEM was operated in low-vacuum mode. Crystals were mounted on an SEM stub with carbon tape and analyzed using a 20 kV accelerating voltage and an 80 s accumulation time. The results of EDS confirmed the presence of elements found by single-crystal X-ray diffraction and did not reveal the presence of any additional elements.

RESULTS AND DISCUSSION

Synthesis

The mild hydrothermal synthesis method was used to pursue the crystallization of new mixed iodate-sulfate materials. During our previous study, [14] in which we reported the synthesis of several new iodate crystals of compositions $Ln_2(IO_3)_3(IO_4)$ (Ln = La, Nd, Pr), we observed the formation of a by-product, $Sm(IO_3)(SO_4)$, when concentrated H_2SO_4, in addition to the iodic acid, was added to the reaction mixture. However, only a couple of crystals could be isolated from those reactions. Optimization to yield pure iodate sulfate products proofed difficult as varying the amount of concentrated H_2SO_4 resulted in mixtures of products, or no crystals at all. When we changed from concentrated H_2SO_4 to diluted H_2SO_4 to adding just 1 mmol H_2SO_4 to the reaction, we obtained $Sm_2(IO_3)_3(SO_4)OH{\bullet}3H_2O$ crystals, albeit, not as a phase pure product. To study the impact on the quantity of SO_4^{2-} in the reaction mixture, further experiments were carried out. After several attempts we determined that the use of Cs_2SO_4 as the SO_4^{2-} source allowed us to crystallize mixed iodate sulfates of the type $Ln_2(IO_3)_3(SO_4)OH{\bullet}3H_2O$ (Ln = Sm, Eu). Since clearly the SO_4^{2-} concentration has a strong effect on the product formation, we continued our investigation and switched from Cs_2SO_4 to 1N H_2SO_4 to study the impact on the SO_4^{2-} source on crystal growth. Varying amounts of (0.1 mL to 2.5 mL) 1N H_2SO_4 were used in the experiments. While $Sm(IO_3)_3$ crystallizes when 0.1 mL of 1N H_2SO_4 is used in the reaction, increasing proton concentration by adjusting the volume of 1N H_2SO_4 to between 1 mL and 1.5

mL, leads to the formation of $Sm_2(IO_3)_3(SO_4)OH•3H_2O$, which contains a hydroxide group. Further increases to 2.5 mL of 1N H_2SO_4 in the reaction, however, results in the simple known iodate, $Sm(IO_3)_3$, as did volumes of less than 1 mL of 1 N H_2SO_4. Such behavior indicates a delicate balance between pH of the starting reaction and the concentration of SO_4^{2-} anions under mild hydrothermal conditions. Interestingly, in our attempts to prepare the dysprosium analog, we found that 2 mL of 1N H_2SO_4 resulted in $Dy_2(IO_3)_3(SO_4)OH•3H_2O$ crystals. The result of varying the sulfate concentration is compiled in Table 2.

Table 2. Effect of H_2SO_4 on the crystal structure

Sm_2O_3 (1mmol) + HIO_3 (3mmol) + H_2O + H_2SO_4 (1N)	
H_2SO_4 (1N)	
0.1 mL	$Sm(IO_3)_3$
1 mL	$Sm_2(IO_3)_3(SO_4)OH•3H_2O$
1.5 mL	$Sm_2(IO_3)_3(SO_4)OH•3H_2O$
2 mL	$Sm(IO_3)_3$ and $Sm_2(IO_3)_3(SO_4)OH•3H_2O$
2.5 mL	$Sm(IO_3)_3$

Lu et al. worked on the crystallization of iodate- sulfate mixed-anion system developed for lanthanide separation.[15] In their work, prisms of *Ln*$(IO_3)(SO_4)$ (*Ln* = La–Gd, except Pm) and blocks of *Ln*$(IO_3)(SO_4)(H_2O)_2•H_2O$ (*Ln* = Tb–Lu) were isolated.

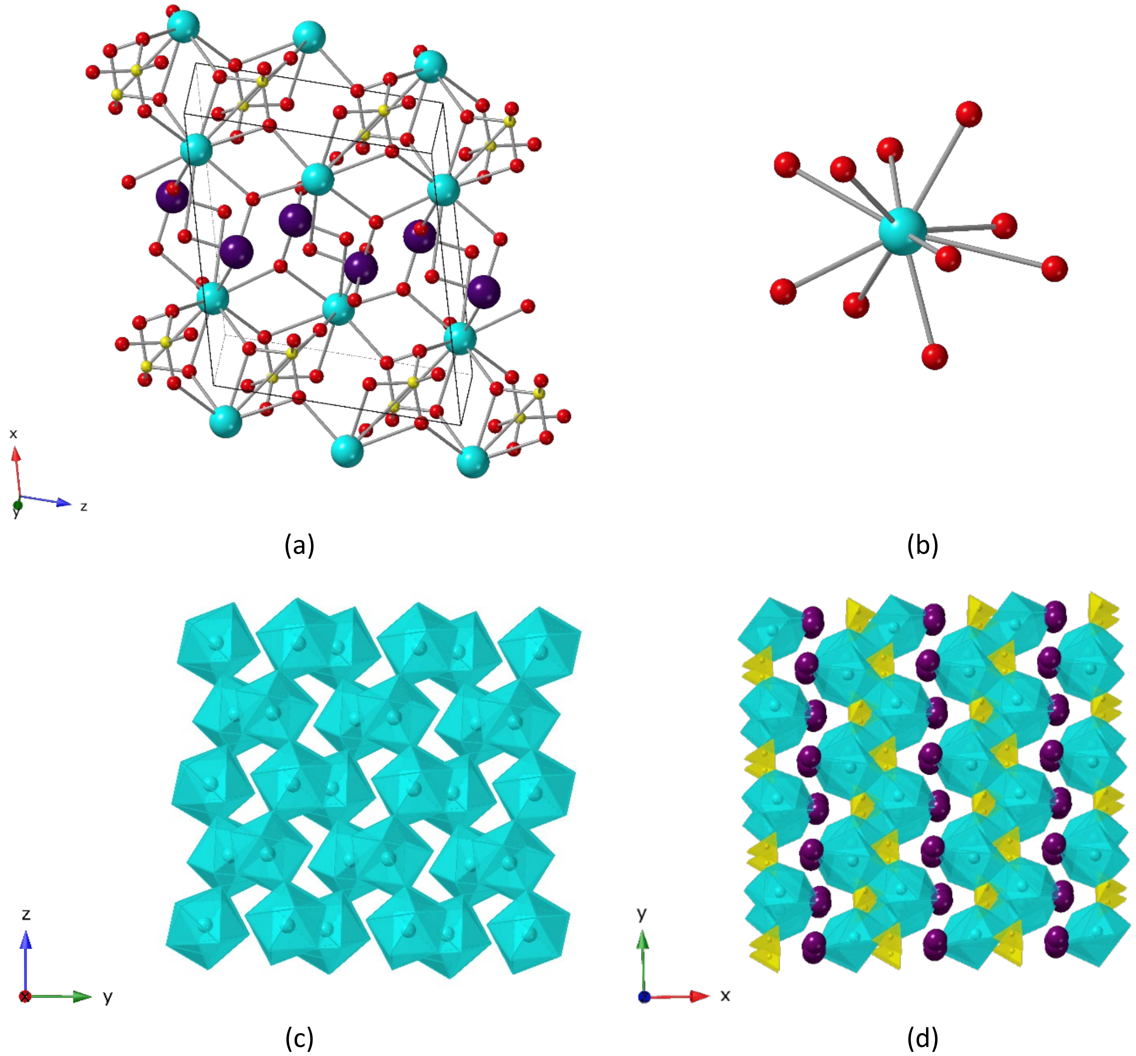
Crystal Structures

$Sm(IO_3)(SO_4)$ (**1**) is isostructural with $Bi(IO_3)(SO_4)$,[12] *Ln*$(IO_3)(SO_4)$ (*Ln* = La–Gd, except Pm)[15] and *Ln*$(IO_3)(SeO_4)$ (Ln = La–Nd) [9] and crystallizes in the centrosymmetric monoclinic space group $P\ 2_1/c$ (Figure 1a). The asymmetric unit contains one IO_3^- anion, one SO_4^{2-} anion and one Sm^{3+} cation. The SmO_{10} polyhedra share edges to form layers in the *bc* plane. (Figure 1c). Each Sm atom is coordinated by four oxygen atoms from IO_3^- anions and six oxygen atoms from

SO_4^{2-} anions (Figure 1b) with an average Sm−O bond length of 2.54 Å (Table S5). The layers are connected into a framework by bridging IO_3^- anions.

Ln$_2$(IO$_3$)$_3$(SO$_4$)OH•3H$_2$O (*Ln* = Sm, Eu, Dy) (**1-3**) crystallize in a new structure type (Figure 2) in the centrosymmetric triclinic space group $P\bar{1}$. The structure contains two *Ln* cations, three I atoms, and seventeen O atoms. The coordination polyhedra of *Ln*1 and *Ln*2 cations are irregular with coordination numbers of 8 and 9 and Sm−O distances in the range of 2.272(3)−2.678(3) Å. *Ln*1O$_8$ polyhedra share edges with neighboring *Ln*2O$_9$ polyhedra. The I atoms connect to the *Ln* atoms via bridging oxygen atoms with I−O distances ranging from 1.791(3) to 1.820(2) Å. SO_4 groups are corner share with both SmO_8 and SmO_9 polyhedra. All bond lengths and atomic coordinates are listed in Tables S1-S8 in the Supporting Information.

The main feature of *Ln*$_2$(IO$_3$)$_3$(SO$_4$)OH•3H$_2$O series is the presence of hydroxide group that results from partial acid neutralization with starting *Ln*$_2$O$_3$ oxides. The hydroxide groups bind two *Ln* atoms each, forming two short Ln–O bonds, 2.270(3) and 2.292(3) Å in the Sm analog. For comparison, the water molecule that is also bound by two neighboring *Ln* atoms forms much longer *Ln*–O bonds, 2.536(3) and 2.665(3) Å for *Ln* = Sm, whereas Sm–O bond length with a terminal water molecule has an intermediate length of 2.413(3) Å. Therefore, crystallographic data confirms the presence of hydroxide groups, which is requires by charge balance, and allows for distinguishing water molecules and hydroxide groups by Ln–O bond lengths.



(a)

(b)

(c)

(d)

Figure 1. (a) Ball-and-stick representation of Sm(IO$_3$)(SO$_4$), (b) SmO$_{10}$, (c) and (d) polyhedral views of the structure of Sm(IO$_3$)(SO$_4$). Sm in blue (ball and stick model), I in purple, O in red, S in yellow.

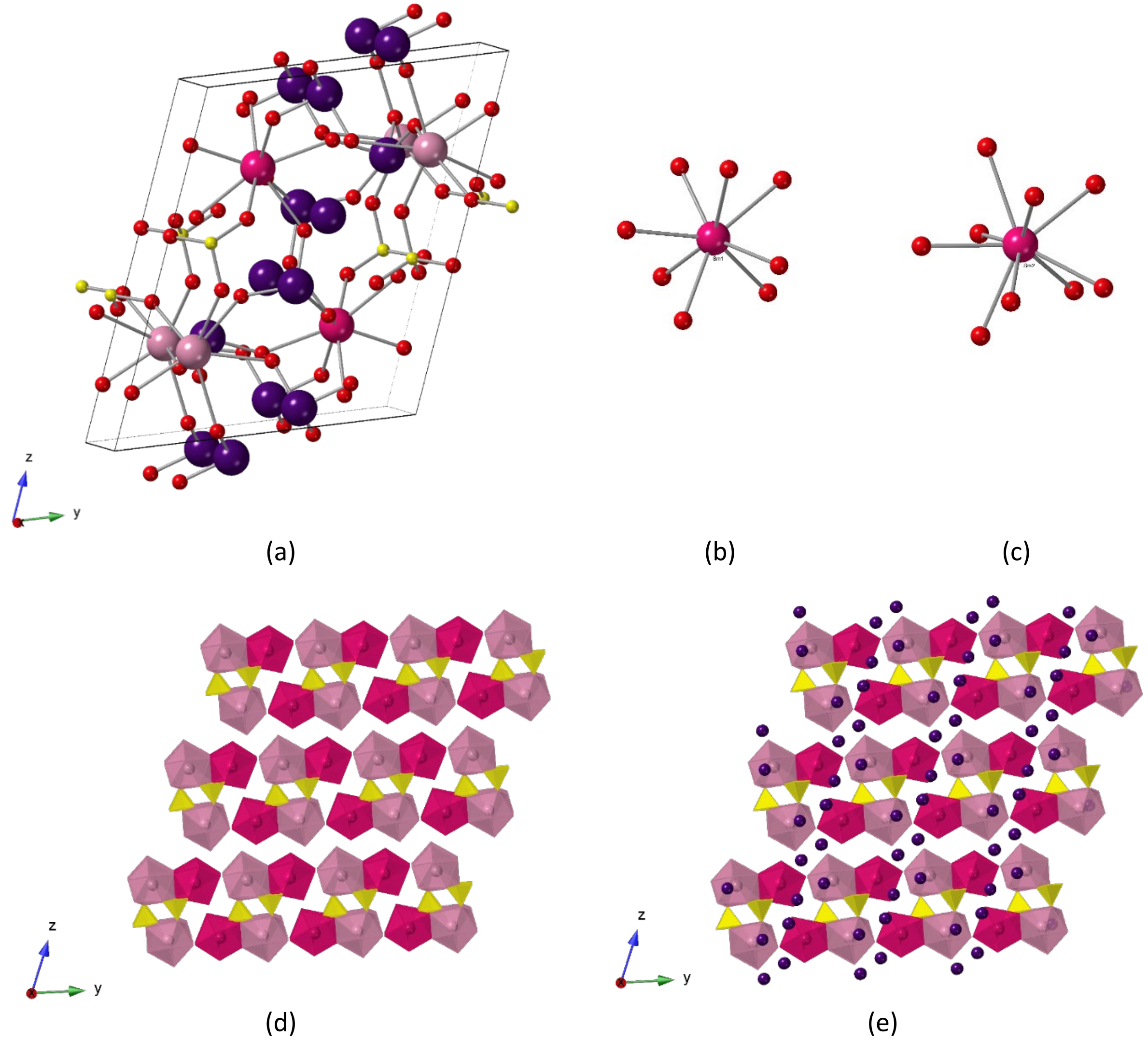


Figure 2. (a) Ball-and-stick representation of $Sm_2(IO_3)_3(SO_4)OH{\bullet}3H_2O$, (b) SmO_8, (c) SmO_9 (d) and (e) polyhedral views of the structure of $Sm_2(IO_3)_3(SO_4)OH{\bullet}3H_2O$. Sm1 in magenta, Sm2 in pink, I in purple, O in red, S in yellow.

Conclusions

Single crystals of iodate sulfates $Sm(IO_3)(SO_4)$ and $Ln_2(IO_3)_3(SO_4)OH{\bullet}3H_2O$ (*Ln* = Sm, Eu, Dy) were grown via mild hydrothermal route and their structures were studied suing single crystal X-ray diffraction. The phase equilibrium in the reaction mixtures was found to be very sensitive to the SO_4^{2-} concentrations and starting pH as noted while studying the impact of varying the quantities of reagents in the reaction mixture. Addition of 0.1 mL or 2.5 mL of 1N H_2SO_4 to the starting reaction results in the formation of $Sm(IO_3)_3$, whereas intermediate quantities of 0.1N H_2SO_4, 1 and 1.5 mL, lead to the formation of $Sm_2(IO_3)_3(SO_4)OH\cdot3H_2O$. All compounds crystallize in centrosymmetric space groups, $P\bar{1}$ for $Sm(IO_3)(SO_4)$ and $P2_1/c$ for $Ln_2(IO_3)_3(SO_4)OH\cdot3H_2O$ (*Ln* = Sm, Eu, Dy).

Acknowledgements

Financial support for this work provided by the National Science Foundation under DMR-1806279 is gratefully acknowledged.

Supporting Information

The Supporting Information is available free of charge at ???

PXRD plot, SEM crystal images, EDS plots, crystallographic tables

Accession Codes

CCDC 2166308-2166311 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

1. Oh, S.-J., H.-G. Kim, H. Jo, T. G. Lim, J. S. Yoo, and K. M. Ok. “Photoconversion Mechanisms and the Origin of Second-Harmonic Generation in Metal Iodates with Wide Transparency, $NaLn(IO_3)_4$ (Ln = La, Ce, Sm, and Eu) and $NaLa(IO_3)_4:Ln^{3+}$ (Ln = Sm and Eu)”, *Inorg. Chem.,* **2017**, *56*, 6973-6981.
2. Nguyen, S. D., Y. Yeon, S.-H. Kim, and P. S. Halasyamani. “$BiO(IO_3)$: A New Polar Iodate that Exhibits and Aurivillius-Type $(Bi_2O_2)^{2+}$ Layer and a Large SHG Response”, *J. Am. Chem. Soc.,* **2011**, *133*, 12422-12425.
3. Park, G., H. R. Byun, J. I. Jang, and K. M. Ok. “Dimensionality-Band Gap-Third-Harmonic Generation Property Relationship in Novel Main-Group Metal Iodates”, *Chem. Mater.,* **2020**, *32*, 3621-3630.
4. Zhang, X.-H., B.-P. Yang, J. Chen, C. L. Hu, Z. Fang, Z. Wang, and J. G. Mao. “A new iodate-phosphate $Pb_2(IO_3)(PO_4)$ achieving great improvements in birefringence activated by $(IO_3)^-$ groups”, *Chem. Commun.,* **2020**, *56*, 635-638.
5. Mao, F.-F., C. L. Hu, J. Chen, and J. G. Mao. “A Series of Mixed Metal Germanium Iodates as Second-Order Nonlinear Optical Materials”, *Chem. Mater.,* **2018**, *30*, 2443-2452.
6. Taouti, M. B., Y. Suffren, O. Leynaud, D. Benbertal, A. Brenier, and I. Gautier-Luneau. “Structures, Thermal Behaviors, and Luminescent Properties of Anhydrous Lanthanum Iodate Polymorphs”, *Inorg. Chem.,* **2015**, *54*, 3608-3618.
7. Xiao, L., F. You, P. Gong, Z. Hu, and Z. Lin. “Synthesis and structure of a new mixed metal iodate $Ba_3HGa_2(IO_3)_{12}$”, *CrystEngComm,* **2019**, *21*, 4981-4986.
8. Phanon, D., A. Mosset, and I. Gautier-Luneau. “New materials for infrared non-linear optics. Syntheses, structural characterizations, second harmonic generation and optical transparency of $M(IO_3)_3$”, *J. Mater. Chem.,* **2007**, *17*, 1123-1130.
9. Qie, M., J. Lin, F. Kong, M. A. Silver, Z. Yue, X. Wang, L. Zhang, H. Bao, T. E. Albrecht-Schmitt, and J. Q. Wang. “A Large Family of Centrosymmetric and Chiral f-Element-Bearing Iodate Selenates Exhibiting Coordination Number and Dimensional Reductions”, *Inorganic Chemistry,* **2018**, *57*, 1676-1683.
10. Regny, S., Y. Suffren, O. Leynaud, I. Gautier-Luneau, and G. Dantelle. “Evidence of reaction intermediates in microwave-assisted synthesis of SHG-active a-$La(IO_3)_3$ nanocrystals”, *CrystEngComm,* **2020**, *22*, 2517-2525.
11. Ding, M., H. Yu, Z. Hu, J. Wang, and Y. Wu. “$Na_7(IO_3)(SO_4)_3$: The first noncentrosymmetric alkaline-metal iodate-sulfate with isolated $[IO_3]$ and $[SO_4]$ units”, *Chemical Communications,* **2021**, *57*, 9598-9601.
12. Li, Y., C. Hu, J. Chen, and J. Mao. “Two bismuth iodate sulfates with enhanced optical anisotropy”, *Dalton Transactions,* **2021**, *50*, 16139-16146.
13. Wu, T., X. Jiang, Y. Zhang, Z. Wang, H. Sha, C. Wu, Z. Lin, Z. Huang, X. Long, M. G. Humphrey, and C. Zhang. “From $CeF_2(SO_4).H_2O$ to $Ce(IO_3)_2(SO_4)$: Defluorinated Homovalent Substitution for Strong Second-Harmonic-Generation Effect and Sufficient Birefringence”, *Chemistry of Materials,* **2021**, *33*, 9317-9325.
14. Kutahyali Aslani, C. , V. V. Klepov, M. A. A. Aslani, and H. C. Z. Loye. “Hydrothermal Synthesis of New Iodates $Ln_2(IO_3)_3(IO_4)$ (Ln = La, Nd, Pr) Containing the

Tetraoxoiodate(V) Anion: Creation of Luminescence Properties by Doping with Eu, Dy, and Tb", *Crystal Growth and Design,* **2021**, *21*, 4707-4712.

15. Lu, H., X. Guo, Y. Wang, K. Diefenbach, L. Chen, J. Q. Wang, J. Lin, and S. Wang. "Size-dependent selective crystallization using an inorganic mixed-oxoanion system for lanthanide separation", *Dalton Transactions,* **2019**, *48*, 12808-12811.
16. Saint. "Bruker, APEX3, SAINT+, TWINABS, and SADABS, Bruker AXS Inc., Madison, Wisconsin, USA, 2015",
17. Krause, L., R. Hertbst-Irmer, and G. M. Sheldrick. "Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination.", *J. Appl. Crystallogr.,* **2015**, *48*, 3-10.
18. Dolomanov, O. V., L. J. Bourhis, R. J. Gildea, J. A. K. Howard, and H. Puschmann. "OLEX2: A complete structure solution, refinement and analysis program.", *J. Appl. Crystallogr.,* **2009**, *42*, 339-341.
19. Sheldrick, G. M. "Crystal Structure Refinement with SHELXL", *Acta Crystallogr. Sect. C., Struct.Chem.,* **2015**, *71*, 3-8.