

**Supporting Information for**

**Bi<sub>3</sub>(SeO<sub>3</sub>)<sub>3</sub>(Se<sub>2</sub>O<sub>5</sub>)F: A Polar Bismuth Selenite Fluoride with Polyhedra of Highly Distortive Lone Pair Cations and Strong Second-Harmonic Generation Response**

*Jee Yoon Chung,<sup>1</sup> Hongil Jo,<sup>1</sup> Seongbeom Yeon,<sup>2</sup> Hye Ryung Byun,<sup>3</sup> Tae-Soo You,<sup>2</sup> Joon I. Jang,<sup>3</sup> and Kang Min Ok<sup>1,\*</sup>*

<sup>1</sup>Department of Chemistry, Sogang University, Seoul 04107, Republic of Korea

<sup>2</sup>Department of Chemistry, Chungbuk National University, Cheongju 28644, Republic of Korea

<sup>3</sup>Department of Physics, Sogang University, Seoul 04107, Republic of Korea

\*E-mail: kmok@sogang.ac.kr

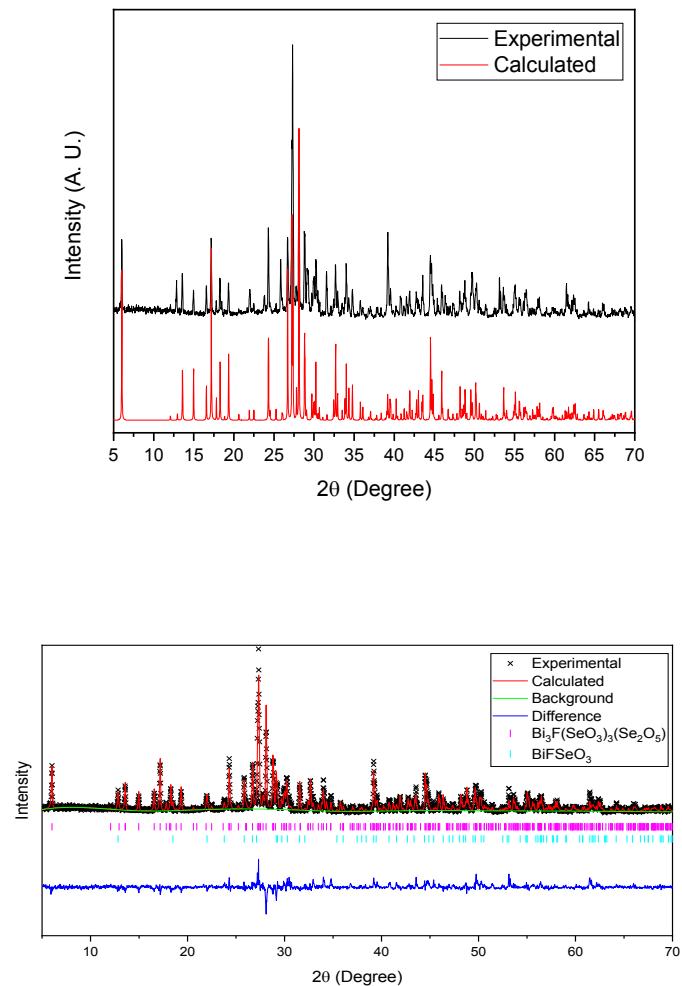
**Table of contents**

Section	Title	page
Table S1	Bond Valence Sum Calculation Result for Bi <sub>3</sub> (SeO <sub>3</sub> ) <sub>3</sub> (Se <sub>2</sub> O <sub>5</sub> )F	S2
Figure S1	Experimental and Calculated Powder X-ray Diffraction Patterns and Final Rietveld plot for Bi <sub>3</sub> (SeO <sub>3</sub> ) <sub>3</sub> (Se <sub>2</sub> O <sub>5</sub> )F	S3
Figure S2	EDX Spectrum for Bi <sub>3</sub> (SeO <sub>3</sub> ) <sub>3</sub> (Se <sub>2</sub> O <sub>5</sub> )F	S4
Figure S3	IR spectrum for Bi <sub>3</sub> (SeO <sub>3</sub> ) <sub>3</sub> (Se <sub>2</sub> O <sub>5</sub> )F	S5
Figure S4	TGA Diagram for Bi <sub>3</sub> (SeO <sub>3</sub> ) <sub>3</sub> (Se <sub>2</sub> O <sub>5</sub> )F and PXRD Patterns for the Products Measured at Different Temperatures	S6
Figure S5	Local Coordination Geometries around O Atoms in Bi <sub>3</sub> (SeO <sub>3</sub> ) <sub>3</sub> (Se <sub>2</sub> O <sub>5</sub> )F	S7

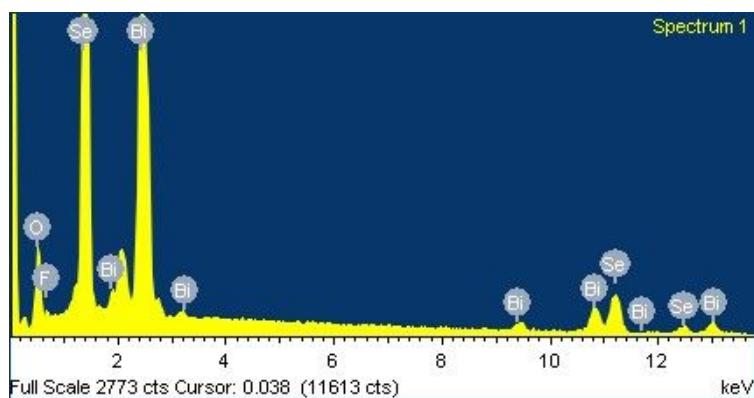
**Table S1.** Bond Valence Sum Calculation Result for  $\text{Bi}_3(\text{SeO}_3)_3(\text{Se}_2\text{O}_5)\text{F}$

$\text{Bi}_3(\text{SeO}_3)_3(\text{Se}_2\text{O}_5)\text{F}$	
Bi1	2.98
Bi2	2.97
Bi3	3.19
Se1	4.10
Se2	3.92
Se3	4.09
Se4	4.05
Se5	3.79
F1	0.96
O1	2.04
O2	2.07
O3	1.89
O4	2.14
O5	2.06
O6	1.88
O7	2.22
O8	1.91
O9	1.88
O10	2.03
O11	2.11
O12	2.00
O13	1.99
O14	1.92

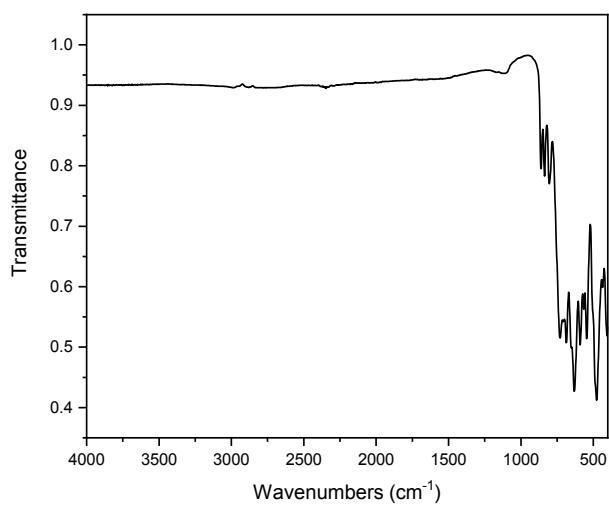
**Figure S1.** Powder X-ray Diffraction Patterns and Final Rietveld plot for  $\text{Bi}_3(\text{SeO}_3)_3(\text{Se}_2\text{O}_5)\text{F}$



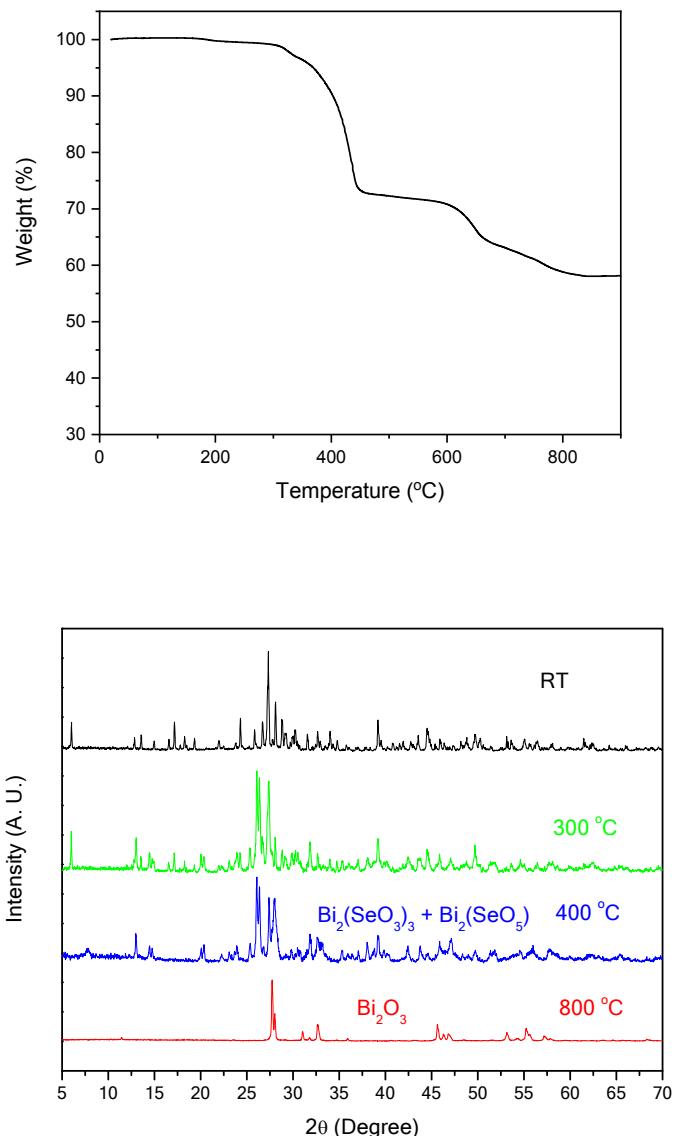
**Figure S2.** EDX Spectrum for  $\text{Bi}_3(\text{SeO}_3)_3(\text{Se}_2\text{O}_5)\text{F}$



**Figure S3.** IR spectrum for  $\text{Bi}_3(\text{SeO}_3)_3(\text{Se}_2\text{O}_5)\text{F}$



**Figure S4.** TGA Diagram for  $\text{Bi}_3(\text{SeO}_3)_3(\text{Se}_2\text{O}_5)\text{F}$  and PXRD Patterns for the Products Measured at Different Temperatures



**Figure S5.** Local Coordination Geometries around O Atoms in  $\text{Bi}_3(\text{SeO}_3)_3(\text{Se}_2\text{O}_5)\text{F}$

