Supporting information

Beryllium-Free Nonlinear Optical Crystals $A_3Ba_3Li_2Ga_4B_6O_{20}F$ (A = K and Rb): Members of $Sr_2Be_2(BO_3)_2O$ Family with Strong Covalent Connection between $^2_\infty[Li_2Ga_4B_6O_{20}F]^{9-}$ Double Layers

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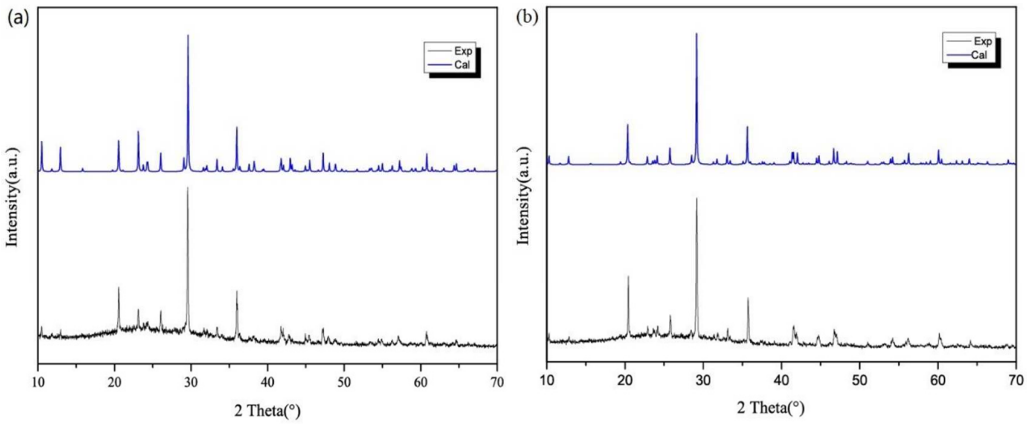

Figure S1. Experimental and calculated powder XRD patterns of (a) I and (b) II.

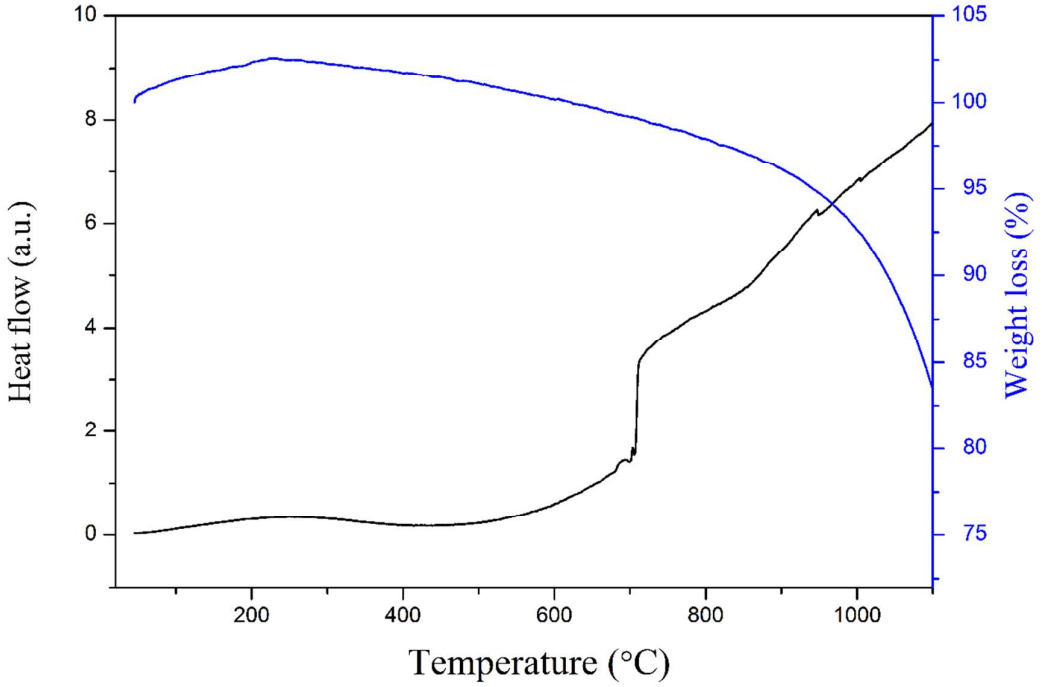

Figure S2. DSC and TGA curves of I.

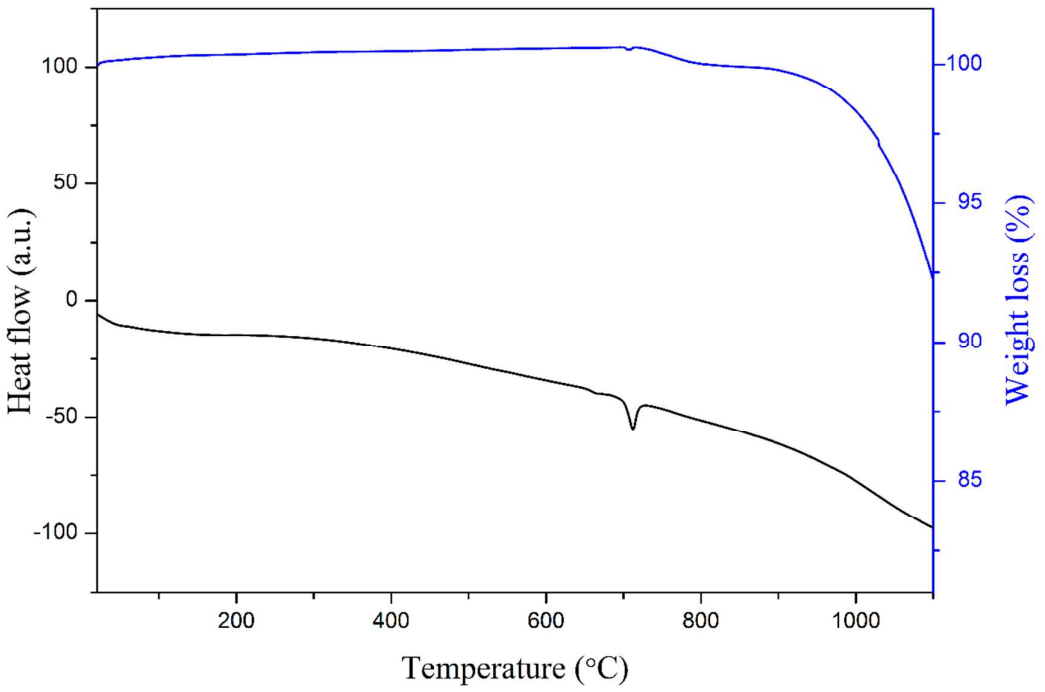

Figure S3. DSC and TGA curves of II.

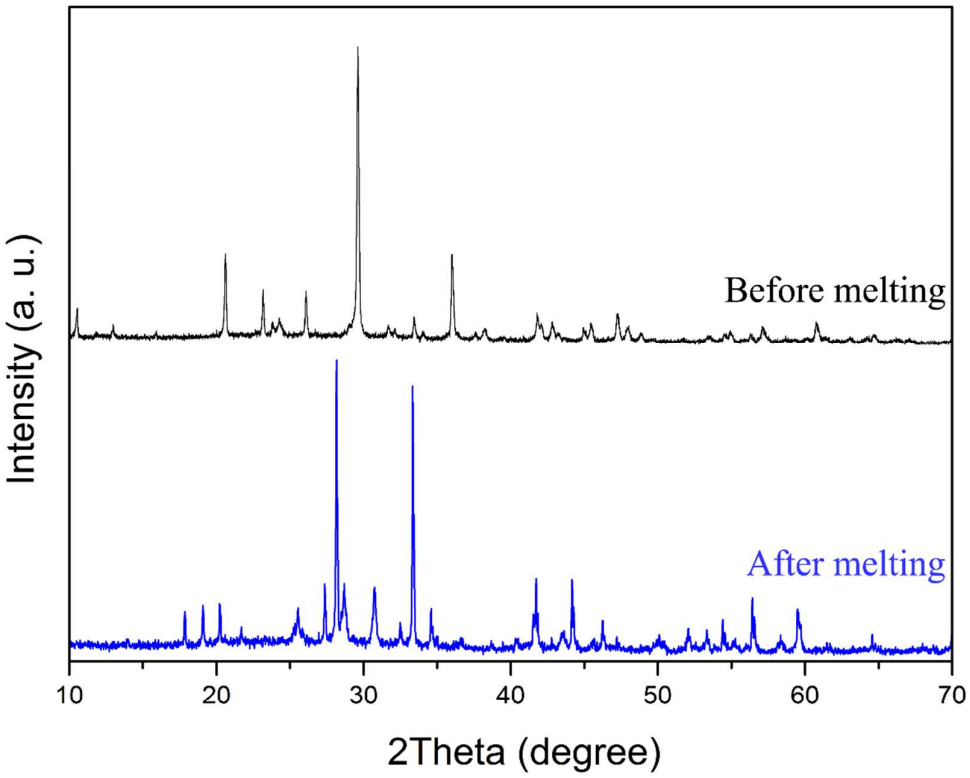

Figure S4. PXRD of I before and after melting.

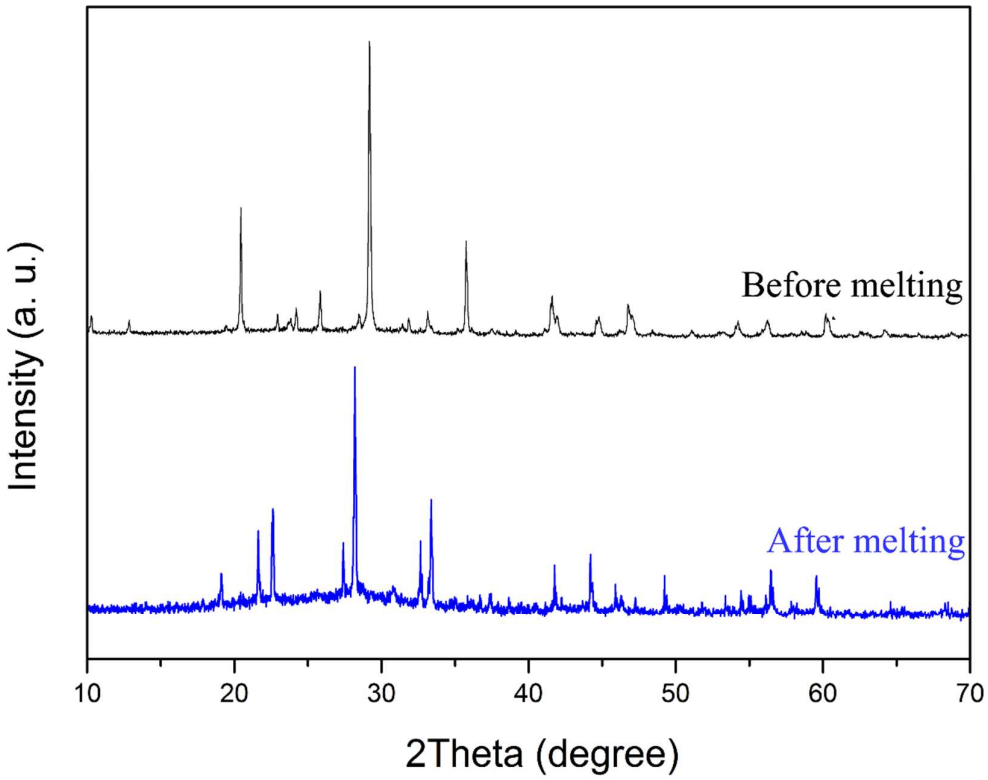

Figure S5. PXRD of II before and after melting.

Table S1. Atom coordinates, equivalent isotropic displacement parameters and bond valence sums (BVS) for I. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	Wyck	Site	x/a	y/b	z/c	U_{eq}	BVS
K1	6h	m..	0.7055(3)	0.0499(3)	1/4	0.0198(8)	0.989
Ba1	6h	m..	0.7055(3)	0.0499(3)	1/4	0.0198(8)	1.409
Ba2	6g	.2.	0.63438(10)	0	0	0.0188(3)	1.722
K2	6g	.2.	0.63438(10)	0	0	0.0188(3)	1.143
Ga1	4f	3..	1/3	-1/3	0.15434(12)	0.0193(5)	3.596
Ga2	4e	3..	0	0	0.10567(13)	0.0106(5)	3.194
B1	12i	1	0.0063(15)	0.3311(18)	0.1181(11)	0.025(3)	2.985
Li1	4f	3..	2/3	1/3	0.1403(16)	0.004(5)	1.125
F1	2d	-6..	2/3	1/3	1/4	0.021(3);	1.134
O1	12i	1	0.0854(9)	0.2292(10)	0.1397(4)	0.0242(16)	1.837
O2	12i	1	0.8375(10)	0.2664(11)	0.0976(5)	0.0296(18)	1.853
O3	12i	1	0.1120(16)	0.5158(15)	0.1293(6)	0.051(2)	1.977
O4	2a	32.	0	0	0	0.067(11)	1.85
O5	2c	-6..	1/3	2/3	1/4	0.58(16)	1.516

Table S2. Atom coordinates, equivalent isotropic displacement parameters and bond valence sums (BVS) for II. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	Wyck	Site	x/a	y/b	z/c	U_{eq}	BVS
Rb1	6h	m..	0.7045(3)	0.0460(3)	1/4	0.0191(4)	0.953
Ba2	6g	.2.	0.63203(13)	0	0	0.0186(3)	1.774
Ga1	4f	3..	1/3	-1/3	0.15281(18)	0.0176(6)	3.354
Ga2	4e	3..	0	0	0.10232(16)	0.0073 (5)	3.28
B1	12i	1	0.015(4)	0.334(3)	0.1176(15)	0.043(6)	2.933
Li1	4f	3..	2/3	1/3	0.142(3)	0.0143(11)	0.941
F1	2d	-6..	2/3	1/3	1/4	0.0157(19)	1.165
O1	12i	1	0.0819(15)	0.2262(17)	0.1352(8)	0.037(3)	2.019
O2	12i	1	0.8382(15)	0.2703(13)	0.0932(6)	0.0216(17)	1.638
O3	12i	1	1.118(2)	0.513(2)	0.1193(8)	0.045(3)	2.211
O4	2a	32.	0	0	0	0.067(10)	2.102
O5	2c	-6..	1/3	2/3	1/4	0.2171(13)	2.354

Table S3. Selected bond distances (Å) and angles (deg) for I.

K1-F1	2.632(2)	Ga1-O3^{6}	1.744(12)
K1-O1^{3}	2.741(7)	Ga1-O3^{7}	1.744(12)
K1-O1^{4}	2.741(7)	Ga1-O5^{8}	1.610(2)
K1-O2^{2}	3.040(9)	Ga2-O1	1.826(7)
K1-O2	3.040(9)	Ga2-O1^{14}	1.826(7)
K1-O3^{5}	3.038(11)	Ga2-O1^{6}	1.826(7)
K1-O5^{6}	3.0389(11)	Ga2-O4	1.778(2)
K1-O5^{7}	3.264(3)	B1-O1	1.405(16)
Ba2-O1^{9}	3.150(8)	B1-O2^{13}	1.321(14)
Ba2-O1^{3}	3.150(8)	B1-O3	1.399(17)
Ba2-O1^{10}	3.211(9)	Li-F1	1.850
Ba2-O2^{11}	3.211(9)	Li-O2^{10}	1.970
Ba2-O2	2.652(7)	Li-O2^{3}	1.970
Ba2-O2^{12}	2.652(7)	Li-O2	1.970
Ba2-O3^{8}	2.776(11)	O1-B1-O2^{13}	125.6(11)
Ba2-O3^{6}	2.776(11)	O3-B1-O2^{13}	118.(12)
Ba2-O4^{1}	3.1589(10)	O3-B1-O1	115.8(10)
Ga1-O3^{3}	1.744(12)		

Symmetry codes: ^{1}1+X,+Y,+Z; ^{2}+X,+Y,1/2-Z; ^{3}1-Y,+X-Y,+Z; ^{4}1-Y,+X-Y,1/2-Z; ^{5}+Y-X,-X,1/2-Z; ^{6}+Y-X,-X,+Z; ^{7}+X,-1+Y,+Z; ^{8}+Y,+X,-Z; ^{9}1-X,-X+Y,-Z; ^{10}1+Y-X,1-X,+Z; ^{11}+Y,-1+X,-Z; ^{12}-Y+X,-Y,-Z; ^{13}-1+X,+Y,+Z; ^{14}-Y,+X-Y,+Z;

Table S4. Selected bond distances (Å) and angles (deg) for II.

Rb1-F1	2686(2)	Ga1-O5^{6}	1.670(3)
Rb1-O1^{1}	2.831(12)	Ga1-O3^{6}	1.770(17)
Rb1-O1^{2}	2.831(12)	Ga1-O3^{3}	1.770(17)
Rb1-O3^{3}	3.241(14)	Ga1-O3^{1}	1.770(17)
Rb1-O3^{4}	3.241(14)	Ga2-O4	1.758(3)
Rb1-O2^{5}	3.187(10)	Ga2-O1	1.820(13)
Rb1-O2	3.187(10)	Ga2-O1^{14}	1820(13)
Rb1-O5^{6}	3.273(2)	Ga2-O1^{3}	1.820(13)
Rb1-O1^{7}	3.468(13)	B1-O3	1.36(3)
Rb1-O1^{8}	3.468(13)	B1-O1	1.36(2)
Ba2-O2	2.667(10)	B1-O2^{15}	1.42(3)
Ba2-O2^{9}	2.667(10)	Li1-F1	1.86(5)
Ba2-O3^{10}	2.721(14)	Li1-O2	2.01(2)
Ba2-O3^{3}	2.721(14)	Li1-O2^{13}	2.01(2)
Ba2-O1^{1}	3.172(14)	Li1-O2^{1}	2.01(2)
Ba2-O1^{11}	3.172(14)	O3-B1-O1	122(2)
Ba2-O2^{12}	3.172(10)	O3-B1-O2^{15}	114.9(17)
Ba2-O2^{13}	3.172(10)	O1-B1-O2^{15}	123.4(19)
Ba2-O4^{8}	3.2093(12)		

Symmetry codes: ^{1}1-Y,+X-Y,+Z; ^{2}1-Y,+X-Y,1/2-Z; ^{3}+Y-X,-X,+Z; ^{4}+Y-X,-X,1/2-Z; ^{5}+X,+Y,1/2-Z; ^{6}+X,-1+Y,+Z; ^{7}1+X,+Y,1/2-Z; ^{8}1+X,+Y,+Z; ^{9}-Y+X,-Y,-Z; ^{10}+Y,+X,-Z; ^{11}1-X,-X+Y,-Z; ^{12}+Y,-1+X,-Z; ^{13}1+Y-X,1-X,+Z; ^{14}-Y,+X-Y,+Z; 15-1+X,+Y,+Z;