Growth and characterization of $Na_3R(BO_3)_2$ (R=La-Gd) borates: crystal structure, high-temperature behavior, and optical properties

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$Na_3R(BO_3)_2$ (R=La-Gd) borates, grown with Na_2O-B_2O_3-NaF flux, crystalize in the space group $P2_1/n$.. Contrary to previously published data the peaks at 980(La)-950(Gd)^oC range are attributed to phase transition process, while melting process occurs around 100^o higher. Another feature of thermal behavior consists in the gradual decomposition of the compound into $Na_3R_2(BO_3)_3$. The end member in decomposition series is $Na_2R_2O(BO_3)_2$ which originates under oxygen/water atmosphere. In addition, the components of the thermal expansion tensor and the dependings of the unit-cell parameters of $Na_3Nd(BO_3)_2$ on temperature were defined. A series of Pr^{3+}, Nd^{3+} and Sm^{3+} doped $Na_3Gd(BO_3)_2$ (NGB) borates were prepared from mixtures of grown crystals by solid-state synthesis and their photoluminescence properties were studied in detail. The excitation and emission spectra of NGB: Pr^{3+} and NGB: Nd^{3+} are comparable with similar compounds, and relative intensity reaches the maximum at 1 mol.% of Pr^{3+}, Sm^{3+} and 10 mol.% for Nd^{3+} doped.

Table S1. Eigenvalues of the thermal expansion tensor $Na_3Nd(BO_3)_3$.

Thermal expansion type	Temperature (°C)								
	100	200	300	400	500	600	700	800	900
α_a (10^{-6} °C^{-1})	5.2)	5.8)	6.5	7.0	7.5	7.9	8.3	8.6	8.9
α_b (10^{-6} °C^{-1})	18.1)	19.3	20.5	21.7	22.9	24.1	25.2	26.4	27.5
α_c (10^{-6} °C^{-1})	28.2	28.7	29.3	30.0	30.7	31.5	32.3	33.3	34.2
α_V (10^{-6} °C^{-1})	26.3	24.2	22.0	19.8	17.6	15.5	13.5	11.5	9.7

Table S2. The final atomic coordinates and displacement parameters of $Na_3Gd(BO_3)_2$ at room temperature.

Atom	x	y	z	Uiso or equiv
Gd1	0.84200(2)	0.386680(17)	0.353185(14)	0.00499(6)
Na1	0.0215(2)	0.18805(16)	0.10149(13)	0.0108(4)
Na2	0.0216(2)	0.76378(17)	0.34527(14)	0.0141(4)
Na3	0.2171(4)	0.5597(2)	0.10638(18)	0.0383(7)
O1	-0.2423(4)	0.6367(2)	0.2523(2)	0.0087(7)
O2	0.1922(5)	0.8429(3)	0.5224(3)	0.0160(8)
O3	0.1785(5)	0.5777(3)	-0.1185(2)	0.0159(8)
O4	0.1714(4)	0.2884(3)	0.2947(3)	0.0139(7)
O5	0.4886(4)	0.3965(3)	0.3684(3)	0.0138(8)
O6	0.1666(4)	0.5158(3)	0.4202(2)	0.0103(7)
B1	0.2817(7)	0.4003(4)	0.3631(4)	0.0072(9)
B2	0.2551(6)	0.9295(5)	0.6283(4)	0.0093(9)

Atom	U_11	U_22	U_33	U_23	U_13	U_12
Gd1	0.00405(10)	0.00518(10)	0.00573(10)	0.00013(4)	-0.00005(6)	-0.00039(4)
Na1	0.0115(7)	0.0117(7)	0.0093(6)	0.0007(5)	0.0009(5)	-0.0030(5)
Na2	0.0150(7)	0.0155(7)	0.0115(7)	-0.0043(6)	-0.0060(5)	0.0021(5)
Na3	0.0779(17)	0.0196(10)	0.0172(9)	0.0111(10)	-0.0084(9)	-0.0038(7)
O1	0.0113(13)	0.0077(11)	0.0070(12)	-0.0004(9)	-0.0022(9)	0.0008(9)
O2	0.0281(16)	0.0096(11)	0.0102(12)	-0.0065(11)	-0.0038(10)	-0.0003(9)
O3	0.0288(16)	0.0094(11)	0.0095(12)	0.0081(11)	0.0009(10)	0.0018(10)
O4	0.0076(11)	0.0154(12)	0.0187(13)	-0.0005(9)	-0.0003(9)	-0.0101(10)
O5	0.0055(12)	0.0182(14)	0.0176(14)	-0.0001(9)	-0.0009(10)	-0.0060(9)
O6	0.0082(11)	0.0104(11)	0.0124(11)	0.0006(9)	0.0004(8)	-0.0036(9)
B1	0.0061(17)	0.0091(16)	0.0065(16)	-0.0006(12)	0.0006(12)	0.0013(11)
B2	0.0101(17)	0.0086(16)	0.0093(16)	-0.0012(13)	-0.0021(12)	-0.0007(13)

Table S3. The final atomic coordinates and displacement parameters of $Na_3Pr(BO_3)_2$ at room temperature.

Atom	x	y	z	Uiso or equiv
Pr1	0.83890(2)	0.386632(18)	0.354355(14)	0.00542(6)
Na1	0.0214(2)	0.19003(16)	0.10343(12)	0.0142(4)
Na2	0.0252(2)	0.76314(16)	0.34210(12)	0.0144(4)
Na3	0.2233(4)	0.5638(2)	0.10686(18)	0.0543(8)
O1	-0.2392(4)	0.6359(2)	0.2464(2)	0.0102(6)
O2	0.1946(5)	0.8479(3)	0.5184(2)	0.0192(8)
O3	0.1870(5)	0.5809(3)	-0.1157(2)	0.0195(8)
O4	0.1729(3)	0.2901(3)	0.2952(2)	0.0133(6)
O5	0.4832(4)	0.3994(3)	0.3682(3)	0.0187(8)
O6	0.1668(3)	0.5190(3)	0.4155(2)	0.0106(6)
B1	0.2793(6)	0.4024(4)	0.3612(3)	0.0080(9)
B2	0.2552(5)	0.9332(4)	0.6244(3)	0.0094(9)

Atom	U_11	U_22	U_33	U_23	U_13	U_12
Pr1	0.00458(10)	0.00552(10)	0.00614(10)	-0.00003(5)	-0.00032(6)	-0.00051(4)
Na1	0.0141(7)	0.0151(7)	0.0134(6)	0.0016(5)	0.0008(5)	-0.0035(5)
Na2	0.0146(7)	0.0156(7)	0.0128(6)	-0.0038(5)	-0.0057(5)	0.0020(5)
Na3	0.124(2)	0.0199(10)	0.0188(8)	0.0168(12)	-0.0150(11)	-0.0045(8)
O1	0.0136(12)	0.0074(10)	0.0095(11)	0.0001(9)	-0.0041(8)	0.0001(8)
O2	0.0384(17)	0.0094(11)	0.0097(11)	-0.0077(11)	-0.0057(10)	0.0006(9)
O3	0.0384(17)	0.0097(11)	0.0104(11)	0.0094(11)	-0.0019(10)	0.0005(9)
O4	0.0075(11)	0.0151(12)	0.0173(10)	-0.0007(9)	-0.0005(8)	-0.0086(9)
O5	0.0075(12)	0.0225(14)	0.0259(14)	0.0002(9)	-0.0018(10)	-0.0096(10)
O6	0.0079(10)	0.0105(11)	0.0134(10)	0.0002(8)	0.0014(8)	-0.0046(8)
B1	0.0068(16)	0.0096(15)	0.0077(14)	-0.0011(11)	0.0009(11)	0.0010(10)
B2	0.0092(16)	0.0083(15)	0.0108(14)	-0.0006(12)	-0.0016(11)	-0.0010(12)

Table S4. The experimental details of the data collection and refinement results of $Na_3Gd(BO_3)_2$ at temperature 400°C.

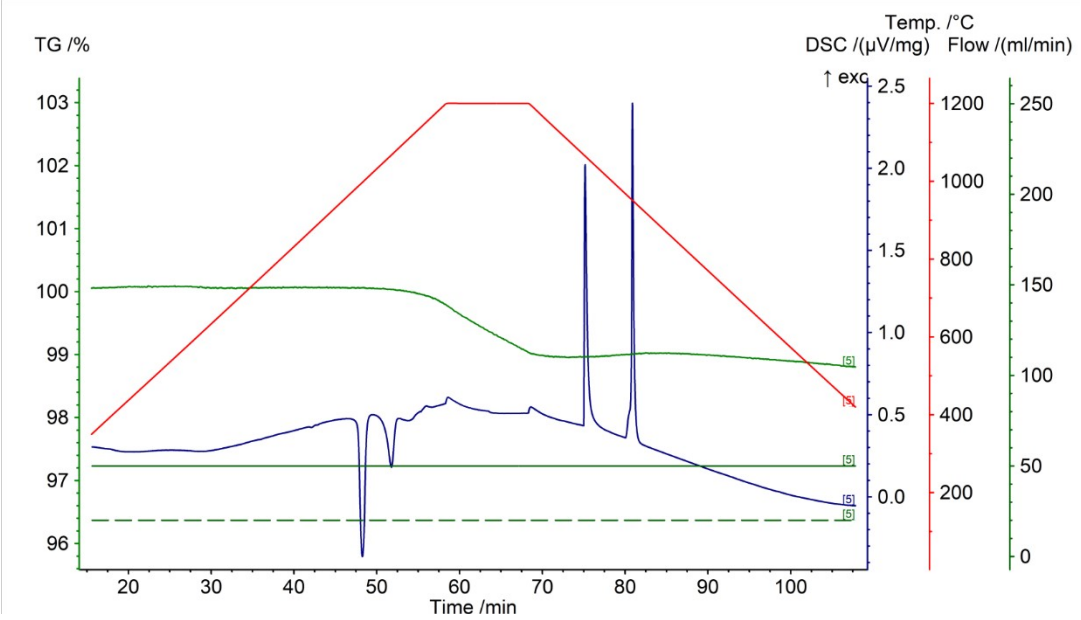
Sample	III
Chemical formula	$Na_3Gd(BO_3)_2$
Formula weight (g)	687.68
Temperature (K)	673
Cell setting	Monoclinic

Space group	$P2_1/n$
a (Å)	6.5511(1)
b (Å)	8.8012(2)
c (Å)	10.2424(1)
β (°)	91.167(2)
V (Å^3)	590.43(2)
Z	2
Calculated density, D_x (g cm^{-3})	3.952
Crystal size (mm)	0.03 × 0.04 × 0.05
Crystal form	Anhedral grain
Data collection	
Diffractometer	Rigaku XtaLAB Synergy, HyPix detector
Radiation; λ	MoK_α; 0.71073
Absorption coefficient, μ (mm^{-1})	11.668
F (000)	620
Data range θ(°); h, k, l	3.658–29.666; $-8 < h < 9$, $-11 < k < 8$, $-14 < l < 14$
No. of measured reflections	7697
Total reflections (N_2) / observed(N_1)	1489 / 1362
Criterion for observed reflections	$I > 3\sigma(I)$
R_{int} (%)	0.0406
Refinement	
Refinement on	Full-matrix least squares on F
Weight scheme	$1/(\sigma^2\|F\|+ 0.0001F^2)$
R_1, wR_1 [$I > 3\sigma(I)$]	0.0196, 0.0434
R_1, wR_1 [all]	0.0237, 0.0455
GooF (Goodness of fit)	1.064
Max./min. residual e density, (eÅ^{-3})	0.958 / –1.081

Tables S5. The final atomic coordinates and displacement parameters of $Na_3Gd(BO_3)_2$ at temperature 400°C.

Atom	x	y	z	Uiso or equiv
Gd1	0.83920(2)	0.11197(2)	0.35224(2)	0.01605(9)
Na1	0.0179(2)	0.30922(18)	0.10039(16)	0.0320(4)
Na2	0.0233(3)	0.7379(2)	0.34709(17)	0.0361(4)
Na3	0.2712(6)	0.4393(3)	0.3943(2)	0.0840(9)
B1	0.2795(7)	0.0989(4)	0.3613(4)	0.0188(8)
B2	0.2548(7)	0.5717(5)	0.6300(5)	0.0226(9)
O1	0.1688(4)	-0.0129(3)	0.4237(3)	0.0307(6)
O2	0.2601(4)	0.6373(3)	0.7529(3)	0.0246(6)
O3	0.1696(4)	0.2056(3)	0.2932(3)	0.0371(7)

O4	0.4855(5)	0.1028(4)	0.3658(4)	0.0389(8)		
O5	0.3130(6)	0.4244(3)	0.6192(3)	0.0379(8)		
O6	0.1923(5)	0.6591(3)	0.5255(3)	0.0363(7)		
Atom	U_11	U_22	U_33	U_23	U_13	U_12
Gd1	0.01551(12)	0.01648(12)	0.01613(13)	0.00082(6)	-0.00014(7)	-0.00041(6)
Na1	0.0325(9)	0.0354(9)	0.0282(9)	0.0048(7)	0.0042(7)	-0.0017(7)
Na2	0.0387(10)	0.0378(9)	0.0312(9)	-0.0029(7)	-0.0133(8)	0.0087(8)
Na3	0.166(3)	0.0451(12)	0.0398(14)	-0.0066(11)	-0.0116(16)	0.0132(16)
B1	0.0187(19)	0.022(2)	0.016(2)	-0.0021(15)	0.0026(16)	-0.0006(15)
B2	0.022(2)	0.0208(19)	0.025(2)	0.0019(17)	-0.0001(17)	0.0012(16)
O1	0.0224(14)	0.0343(15)	0.0354(17)	0.0139(13)	0.0032(12)	-0.0013(11)
O2	0.0326(16)	0.0192(13)	0.0219(15)	-0.0009(11)	-0.0028(12)	-0.0004(11)
O3	0.0197(14)	0.0427(17)	0.049(2)	0.0218(15)	-0.0017(13)	0.0023(12)
O4	0.0158(14)	0.054(2)	0.047(2)	0.0182(15)	0.0008(14)	-0.0002(12)
O5	0.067(2)	0.0222(13)	0.0246(16)	0.0035(12)	0.0002(15)	0.0158(14)
O6	0.063(2)	0.0230(13)	0.0227(15)	0.0026(12)	-0.0091(14)	0.0089(14)



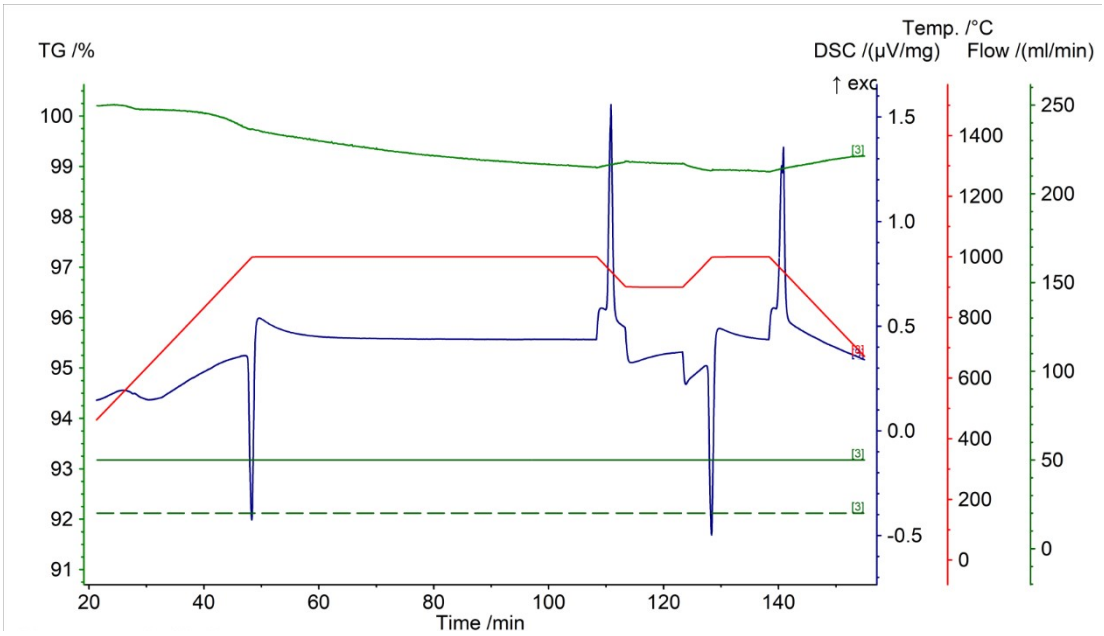


Figure S1. DSC curve of $Na_3Nd(BO_3)_2$

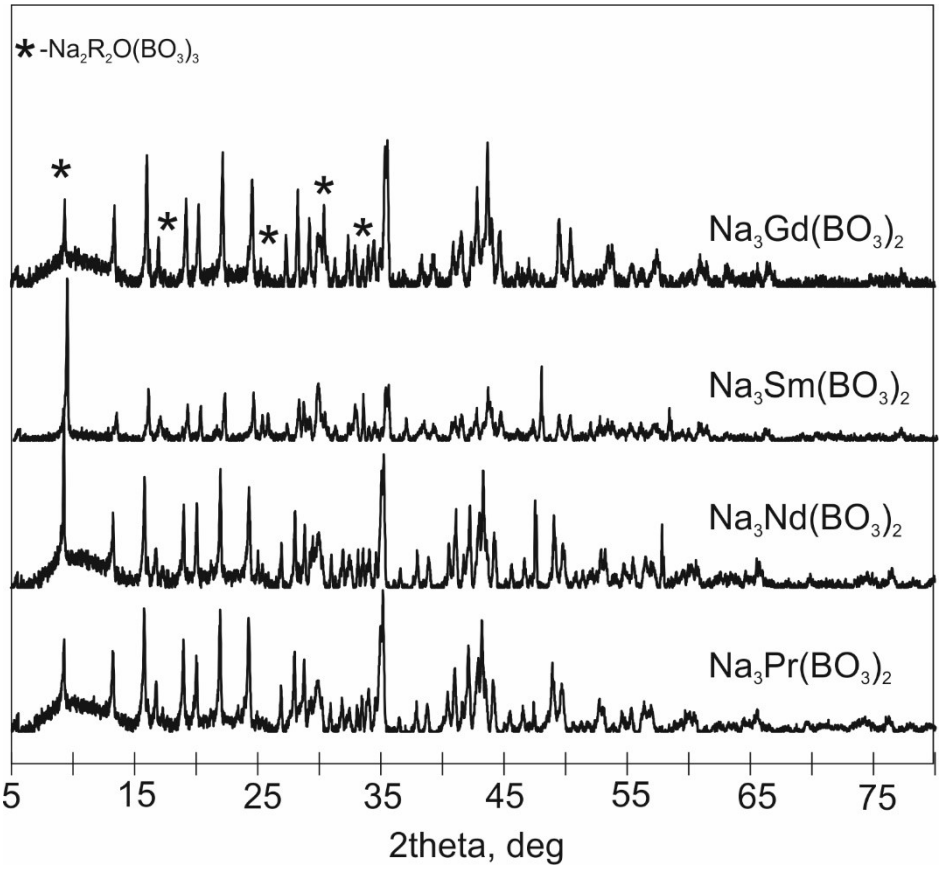


Figure S2. $Na_3R(BO_3)_2$ XRD patterns after heating at 1200°C.

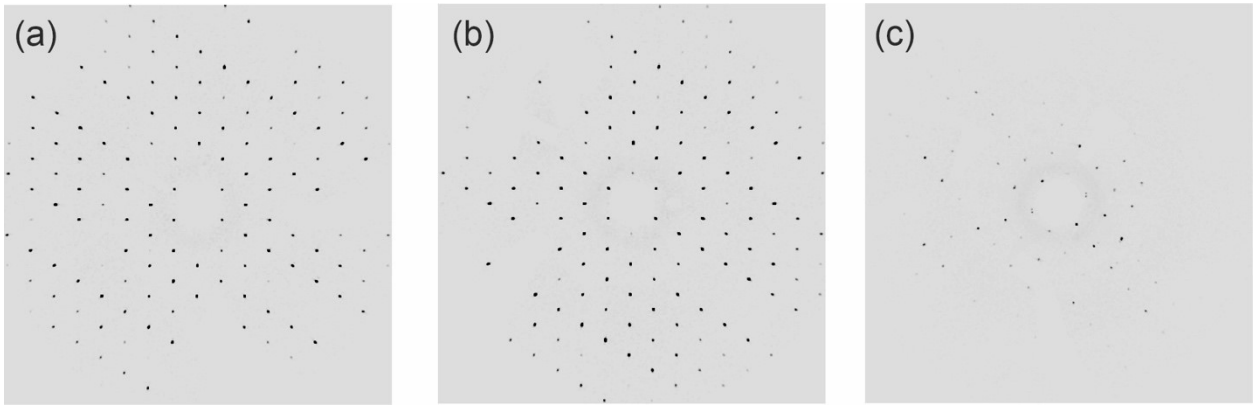


Figure S3. Reciprocal space reconstructions for $Na_3Gd(BO_3)_2$ in the *h0l* plane at 27 °C (a), 600 °C (b) and 800 °C (c).

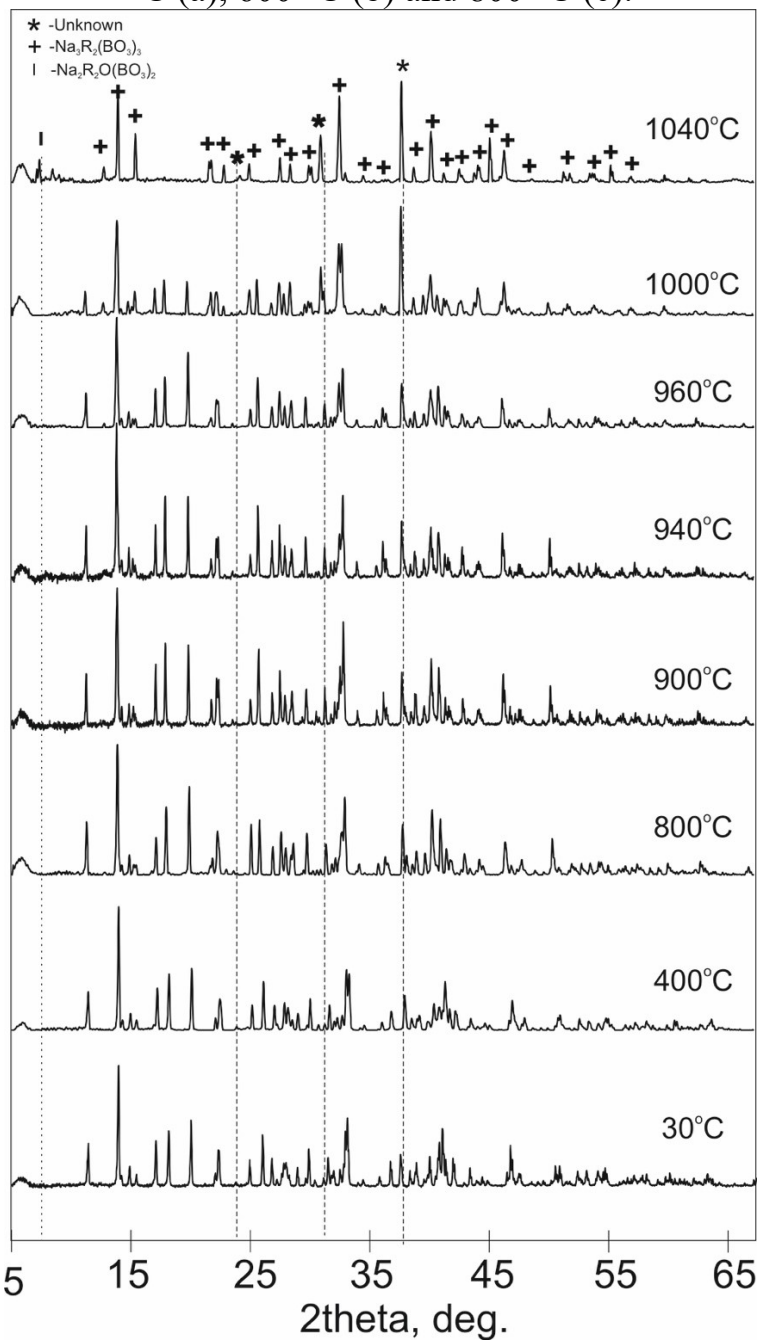


Figure S4. Powder XRD patterns of $Na_3Nd(BO_3)_2$ *in-sity* in temperature range 30-1040°C

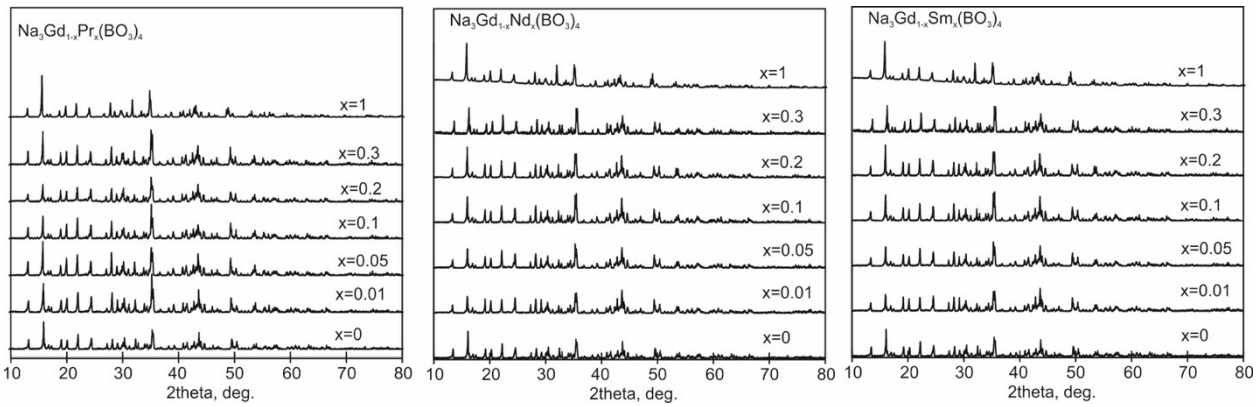


Figure S5. XRD patterns of $Na_3Gd_{1-x}(BO_3)_2$:xPr^{3+}/Nd^{3+}/Sm^{3+} samples

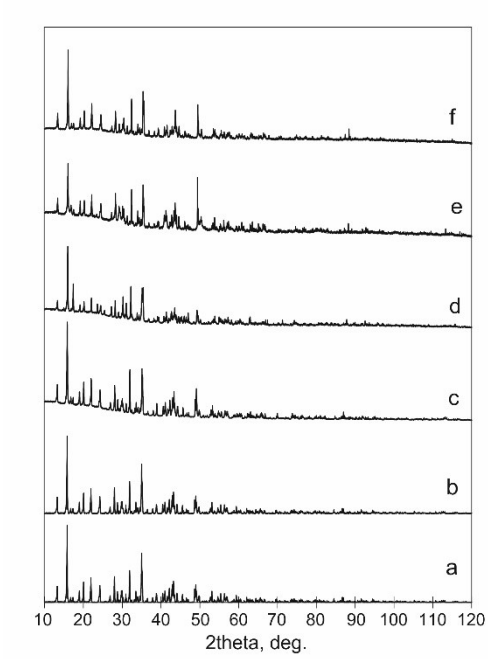


Figure S6. XRD patterns of $Na_3R(BO_3)_3$ R= La(a), Pr(b), Nd(c), Sm(d), Eu(e) and Gd(f).