Supplementary Materials

Novel non-centrosymmetric $NdSr_4O(BO_3)_3$ borate and $Nd(Ca_{1-x}Sr_x)_4O(BO_3)_3$ solid solutions: preparation, crystal structures, thermal expansion and optical properties

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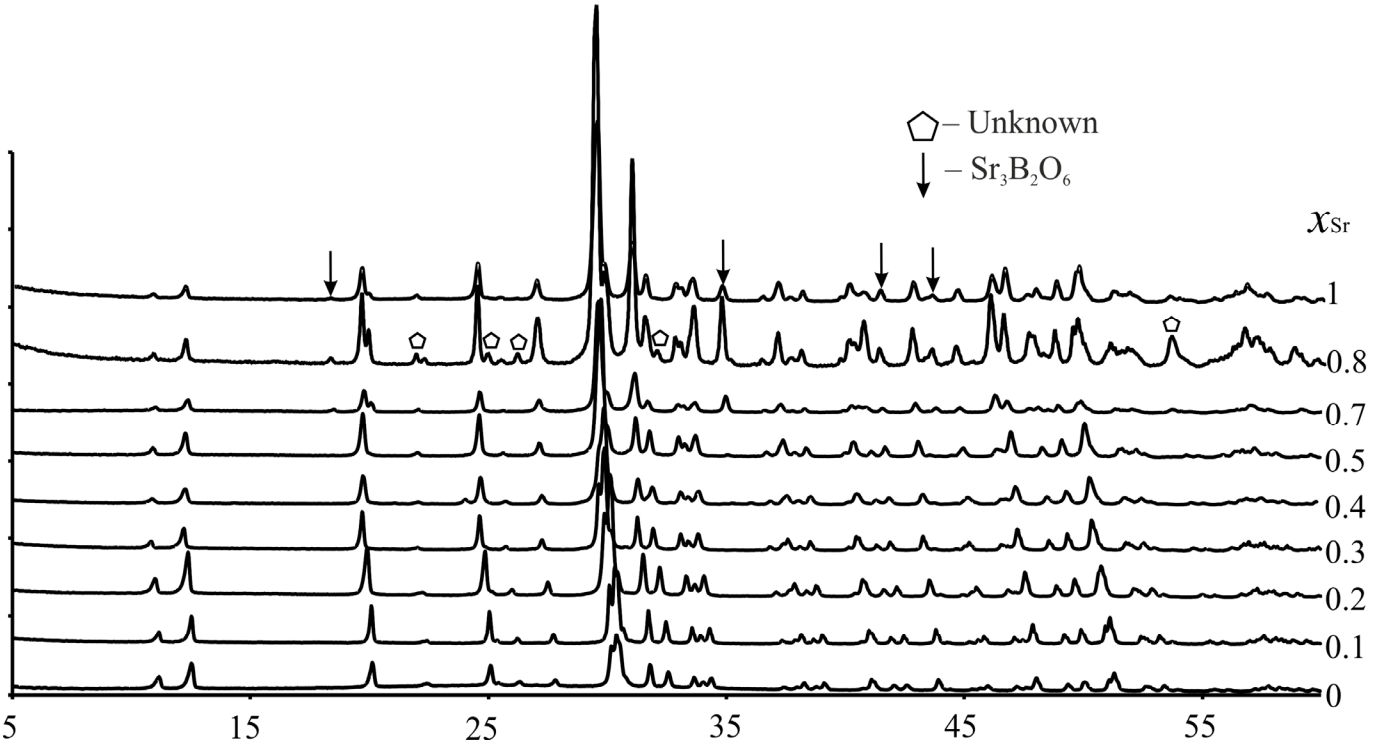

Figure S1. XRD patterns of the $Nd(Ca_{1-x}Sr_x)_4O(BO_3)_3$ solid solutions synthesized at 1300 °C.

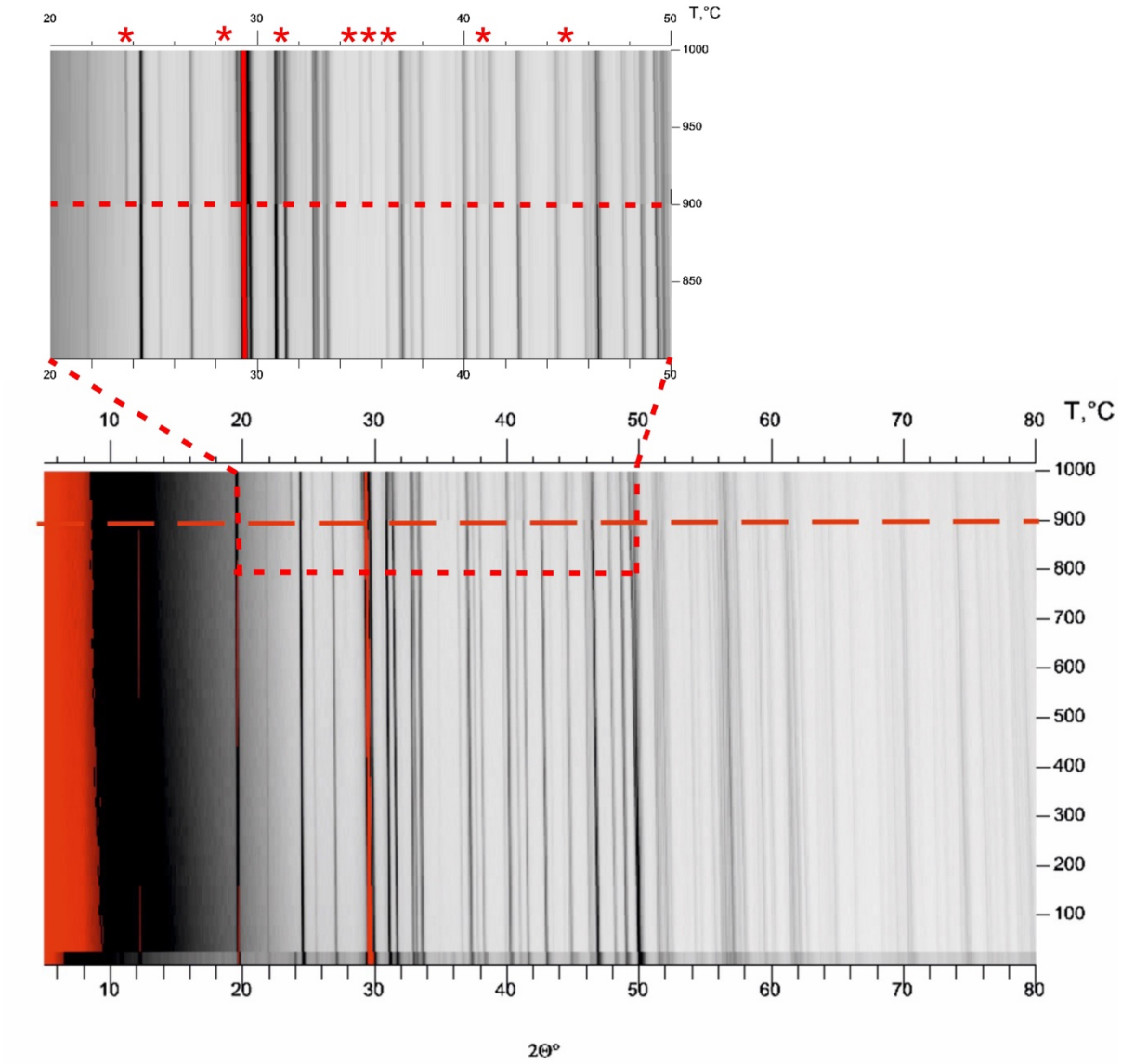

Figure S2. 2D-top view of HTXRD pattern of the sample $(Ca_{0.5}Sr_{0.5})_4NdO(BO_3)_3$. The dotted line indicates the beginning of the appearance of the impurity.

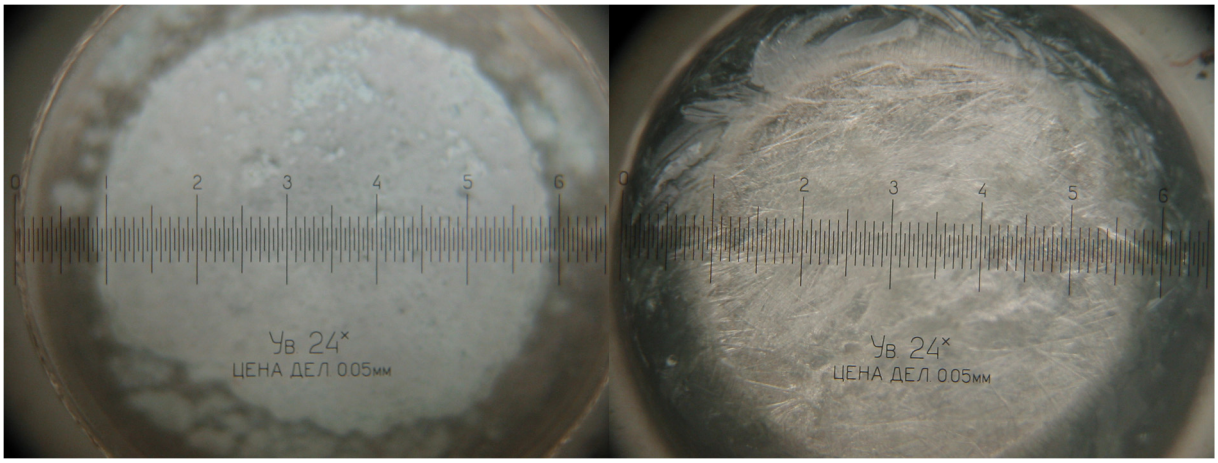

Figure S3. Microphotographs of the tablet in the crucible of $Ca_4NdO(BO_3)_3$ before (left) and after (right) heating to 1445 °C.

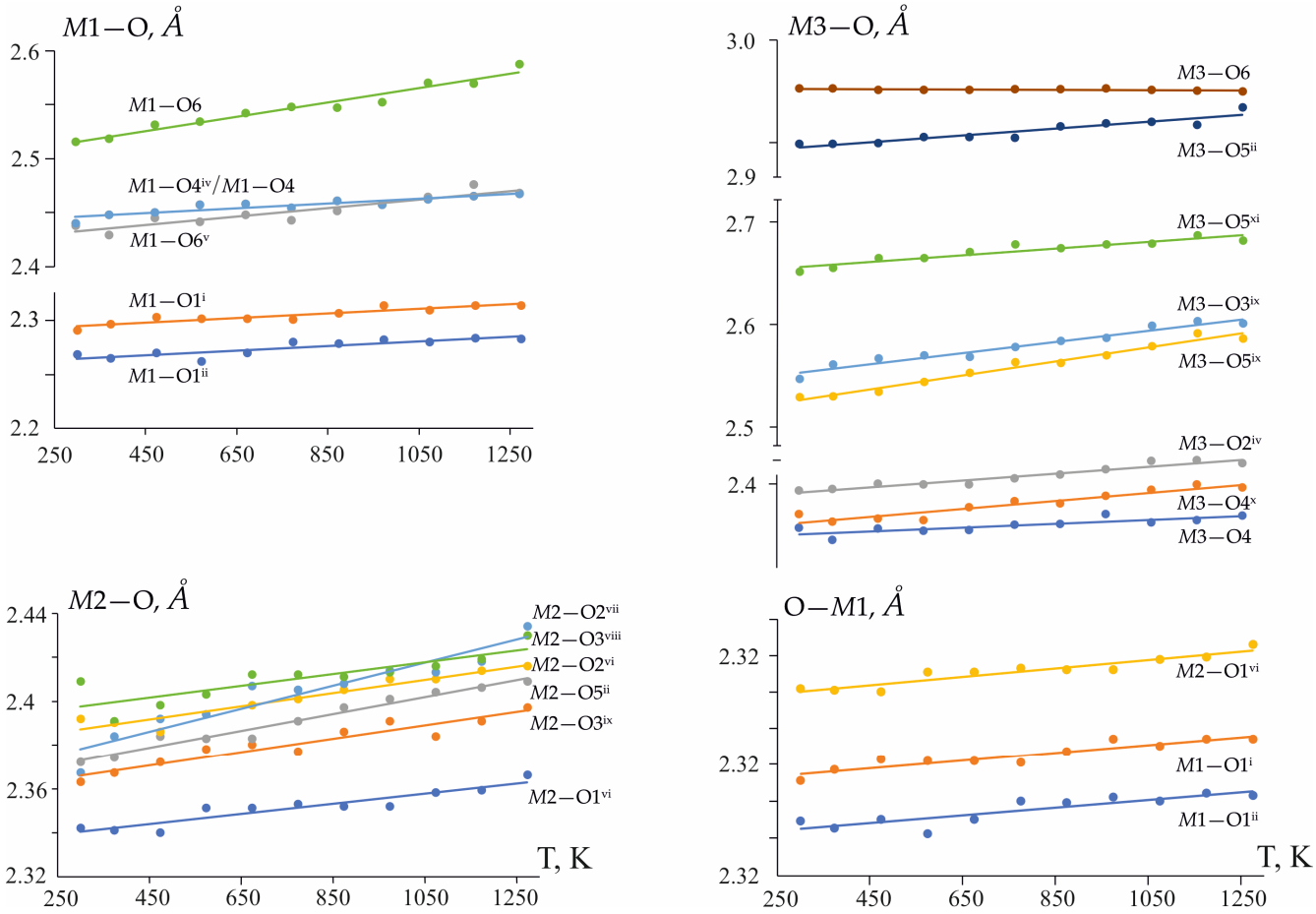

Figure S4. Changes of bond lengths in the cationic *M*1–*M*3 polyhedra and oxy-centered O*M*4 tetrahedra (top left) with increasing temperature.

Table S1. Atomic coordinates, isotropic or equivalent isotropic displacement parameters (Å^2) in the structure of $Nd(Ca_{0.8}Sr_{0.2})_4O(BO_3)_3$.

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Nd1	0.00152 (5)	0	-0.00766 (11)	0.00779 (10)	0,8977
Ca1	0.00152 (5)	0	-0.00766 (11)	0.00779 (10)	0,1023
Ca2	0.14550 (9)	0.38750 (5)	0.3236 (2)	0.0076 (2)	0,8096
Sr2	0.14550 (9)	0.38750 (5)	0.3236 (2)	0.0076 (2)	0,1904
Nd3	0.26439 (5)	0.18051 (5)	0.64796 (12)	0.0103 (2)	0,0511
Ca3	0.26439 (5)	0.18051 (5)	0.64796 (12)	0.0103 (2)	0,7393
Sr3	0.26439 (5)	0.18051 (5)	0.64796 (12)	0.0103 (2)	0,2096
O1	0.8274 (7)	0	0.4132 (16)	0.0082 (14)	
O2	0.4694 (5)	-0.0734 (2)	0.7454 (11)	0.0145 (11)	
O3	0.7984 (5)	0.1713 (3)	0.8861 (11)	0.0148 (11)	
O4	0.0906 (5)	0.1443 (3)	0.0729 (11)	0.0151 (12)	
O5	0.9708 (5)	0.2688 (2)	0.2640 (11)	0.0152 (11)	
O6	0.2115 (7)	0	0.6034 (17)	0.0164 (18)	
B1	0.3823 (10)	0	0.697 (2)	0.0067 (19)	
B2	0.9542 (7)	0.1944 (4)	0.0752 (16)	0.0080 (14)	

Table S2. Atomic coordinates, isotropic or equivalent isotropic displacement parameters (Å²) and in the structure of $Nd(Ca_{0.5}Sr_{0.5})_4O(BO_3)_3$.

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Nd1	0.00318 (7)	0	-0.00499 (16)	0.0087 (2)	0,8728
Ca1	0.00318 (7)	0	-0.00499 (16)	0.0087 (2)	0,1272
Ca2	0.14595 (13)	0.38808 (7)	0.3241 (3)	0.0098 (3)	0,5303
Sr2	0.14595 (13)	0.38808 (7)	0.3241 (3)	0.0098 (3)	0,4697
Nd3	0.26230 (7)	0.18051 (6)	0.64482 (16)	0.0126 (3)	0,0636
Ca3	0.26230 (7)	0.18051 (6)	0.64482 (16)	0.0126 (3)	0,4061
Sr3	0.26230 (7)	0.18051 (6)	0.64482 (16)	0.0126 (3)	0,5303
O1	0.8305 (11)	0	0.418 (3)	0.010 (3)	
O2	0.4678 (8)	-0.0726 (4)	0.7450 (18)	0.020 (2)	
O3	0.7961 (8)	0.1714 (4)	0.8896 (19)	0.019 (2)	
O4	0.0839 (9)	0.1427 (4)	0.073 (2)	0.019 (2)	
O5	0.9710 (8)	0.2671 (4)	0.2662 (18)	0.015 (2)	
O6	0.2116 (12)	0	0.610 (3)	0.019 (3)	
B1	0.3814 (17)	0	0.702 (4)	0.007 (2)*	
B2	0.9485 (12)	0.1938 (6)	0.075 (3)	0.009 (3)	

Table S3. Atomic coordinates, isotropic or equivalent isotropic displacement parameters (Å²) and in the structure of $NdSr_4O(BO_3)_3$.

	x	y	z	U_{iso}*/U_{eq}
Nd1	0.00485 (2)	0	−0.00412 (5)	0.00537 (7)
Sr2	0.14605 (5)	0.38837 (3)	0.32515 (11)	0.01550 (11)
Sr3	0.26167 (4)	0.18132 (3)	0.64490 (10)	0.01194 (10)
O1	0.8350 (6)	0	0.4160 (12)	0.0064 (10)
O2	0.4691 (5)	−0.0721 (2)	0.7423 (12)	0.0158 (9)
O3	0.7964 (4)	0.1716 (2)	0.8911 (11)	0.0133 (8)
O4	0.0824 (4)	0.1415 (2)	0.0646 (10)	0.0107 (8)
O5	0.9751 (4)	0.2658 (2)	0.2606 (9)	0.0102 (8)
O6	0.2153 (6)	0	0.6118 (15)	0.0139 (13)
B1	0.3853 (8)	0	0.7001 (18)	0.0064 (13)
B2	0.9529 (5)	0.1925 (3)	0.0710 (12)	0.0050 (6)*

Table S4. Atomic displacement parameters (Å²) for $Nd(Ca_{0.8}Sr_{0.2})_4O(BO_3)_3$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Nd1	0.00655(16)	0.01267(18)	0.00420(15)	0	0.00117(11)	0
Ca1	0.00655(16)	0.01267(18)	0.00420(15)	0	0.00117(11)	0
Ca2	0.0075(3)	0.0084(4)	0.0069(3)	-0.0010(3)	0.0010(3)	-0.0001(3)

Sr2	0.0075(3)	0.0084(4)	0.0069(3)	-0.0010(3)	0.0010(3)	-0.0001(3)
Nd3	0.0101(3)	0.0138(4)	0.0072(3)	-0.0002(3)	0.0021(3)	-0.0006(2)
Ca3	0.0101(3)	0.0138(4)	0.0072(3)	-0.0002(3)	0.0021(3)	-0.0006(2)
Sr3	0.0101(3)	0.0138(4)	0.0072(3)	-0.0002(3)	0.0021(3)	-0.0006(2)
O1	0.009(2)	0.007(2)	0.009(2)	0	0.0028(19)	0
O2	0.0184(18)	0.0094(17)	0.0155(19)	0.0060(15)	0.0031(15)	0.0004(14)
O3	0.0121(18)	0.022(2)	0.0101(18)	-0.0078(15)	0.0010(14)	-0.0029(14)
O4	0.0167(19)	0.0127(19)	0.017(2)	0.0027(15)	0.0053(15)	0.0010(15)
O5	0.0181(18)	0.0112(17)	0.0179(19)	-0.0030(14)	0.0073(15)	-0.0040(14)
O6	0.006(2)	0.035(4)	0.008(3)	0	0.001(2)	0
B1	0.009(3)	0.008(3)	0.005(3)	0	0.004(3)	0
B2	0.009(2)	0.008(2)	0.007(2)	-0.0025(19)	0.0029(17)	0.0022(18)

Table S5. Atomic displacement parameters (Å^2) for $Nd(Ca_{0.5}Sr_{0.5})_4O(BO_3)_3$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Nd1	0.0079(3)	0.0116(4)	0.0068(3)	0	0.0018(2)	0
Ca1	0.0079(3)	0.0116(4)	0.0068(3)	0	0.0018(2)	0
Ca2	0.0079(6)	0.0112(6)	0.0099(5)	-0.0012(4)	0.0012(4)	-0.0008(4)
Sr2	0.0079(6)	0.0112(6)	0.0099(5)	-0.0012(4)	0.0012(4)	-0.0008(4)
Nd3	0.0113(5)	0.0162(5)	0.0105(5)	-0.0004(4)	0.0027(4)	-0.0008(4)
Ca3	0.0113(5)	0.0162(5)	0.0105(5)	-0.0004(4)	0.0027(4)	-0.0008(4)
Sr3	0.0113(5)	0.0162(5)	0.0105(5)	-0.0004(4)	0.0027(4)	-0.0008(4)
O1	0.006(4)	0.014(5)	0.009(4)	0	0.004(3)	0
O2	0.023(4)	0.013(3)	0.024(4)	0.010(3)	0.003(3)	0.000(3)
O3	0.015(3)	0.027(4)	0.016(3)	-0.010(3)	0.002(3)	-0.002(3)
O4	0.020(4)	0.017(3)	0.023(4)	0.006(3)	0.009(3)	0.004(3)
O5	0.016(3)	0.011(3)	0.020(4)	-0.007(2)	0.004(3)	-0.005(2)
O6	0.003(4)	0.039(7)	0.013(5)	0	-0.004(4)	0
B2	0.006(4)	0.010(4)	0.012(4)	-0.002(3)	0.002(3)	0.004(3)

Table S6. Atomic displacement parameters (Å^2) for $NdSr_4O(BO_3)_3$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Nd1	0.00520(11)	0.00786(12)	0.00329(11)	0	0.00145(7)	0
Sr2	0.01460(19)	0.01601(19)	0.01560(18)	−0.00165(13)	0.00238(15)	−0.00056(14)
Sr3	0.01082(16)	0.01571(18)	0.00937(17)	−0.00086(12)	0.00223(12)	−0.00110(12)
O1	0.0081(16)	0.0086(16)	0.0026(15)	0	0.0017(12)	0
O2	0.0192(16)	0.0064(13)	0.0228(18)	0.0056(12)	0.0062(13)	0.0018(12)
O3	0.0070(12)	0.0185(15)	0.0131(15)	−0.0072(11)	−0.0011(10)	0.0016(11)
O4	0.0094(12)	0.0081(12)	0.0159(15)	0.0038(10)	0.0059(11)	−0.0012(10)
O5	0.0137(13)	0.0088(12)	0.0088(13)	−0.0007(10)	0.0036(10)	−0.0028(10)
O6	0.0035(17)	0.027(3)	0.011(2)	0	0.0000(14)	0
B1	0.009(2)	0.0048(19)	0.006(2)	0	0.0027(17)	0

Table S7. Bond lengths (Å) of $(Ca_{1-x}Sr_x)_4NdO(BO_3)_3$ (x = 0.2, 0.5, 1).

x_{Sr}	0.2	0.5	1	x_{Sr}	0.2	0.5	1
M1—O1^{ii}	2.285(6)	2.318(10)	2.308(5)	M3—O2^{iv}	2.390(4)	2.428(7)	2.468(4)
M1—O1^{i}	2.292(5)	2.307(8)	2.321(4)	M3—O5^{ix}	2.530(5)	2.576(7)	2.583(4)
M1—O6^{v}	2.430(7)	2.446(11)	2.417(3)	M3—O3^{ix}	2.546(4)	2.580(7)	2.643(4)
M1—O4	2.447(4)	2.431(7)	2.417(3)	M3—O5^{xi}	2.649(4)	2.711(6)	2.734(3)
M1—O4^{iv}	2.447(4)	2.431(7)	2.474(6)	M3—O5^{ii}	2.903(4)	2.901(6)	2.877(3)
M1—O6	2.520(6)	2.553(9)	2.580(5)	M3—O6	2.9527(11)	2.9826(16)	3.0078(8)
<M1-O>$_6$	2.404	2.414	2.420	<M3-O>$_8$	2.586	2.628	2.652
M2—O1^{vi}	2.334(4)	2.366(6)	2.398(3)	B1—O2	1.378(5)	1.380(10)	1.369(5)
M2—O3^{ix}	2.369(4)	2.404(7)	2.424(4)	B1—O6	1.373(10)	1.378(17)	1.369(5)
M2—O5^{ii}	2.380(4)	2.436(6)	2.433(5)	B1—O2^{iv}	1.378(5)	1.380(10)	1.387(8)
M2—O2^{vii}	2.381(4)	2.420(6)	2.440(4)	<B1-O>$_3$	1.376	1.379	1.375
M2—O2^{vi}	2.386(4)	2.432(7)	2.443(4)	B2—O3^{v}	1.375(6)	1.358(11)	1.371(6)
M2—O3^{viii}	2.402(4)	2.419(8)	2.452(3)	B2—O4^{xii}	1.377(7)	1.385(12)	1.381(5)
<M2-O>$_6$	2.375	2.413	2.432	B2—O5	1.382(7)	1.401(12)	1.390(5)
M3—O4	2.352(4)	2.396(7)	2.445(3)	<B2-O>$_3$	1.378	1.381	1.381
M3—O4^{x}	2.368(5)	2.446(8)	2.456(4)				

Symmetry codes: (i) x−1, y, z−1; (ii) x−1, y, z; (iii) x, −y, z; (iv) x, y, z−1; (v) x−1/2, y+1/2, z; (vi) x−1/2, y+1/2, z−1; (vii) x−1/2, −y+1/2, z−1; (viii) x−1/2, −y+1/2, z; (ix) x, y, z+1; (x) x−1/2, −y+1/2, z+1; (xi) x+1, y, z.

Table S8. Crystal data and experimental details for structures of $Nd(Ca_{0.8}Sr_{0.2})_4O(BO_3)_3$ in the temperature range 300 – 1273 K.

Crystal data						
M_r	535					
Crystal system, space group	Monoclinic, *Cm*					
Temperature (K)	300	473	673	873	1073	1273
a (Å)	8.1859 (2)	8.1984 (3)	8.2196 (3)	8.2369 (3)	8.2548 (3)	8.2757 (3)
b (Å)	16.1737 (4)	16.1947 (6)	16.2230 (5)	16.2495 (6)	16.2784 (5)	16.3051 (6)
c (Å)	3.6245 (1)	3.6342 (1)	3.6447 (1)	3.6539 (1)	3.6654 (1)	3.67710 (10)
β (°)	101.480 (2)	101.469 (4)	101.515 (4)	101.545 (4)	101.601 (4)	101.636 (4)
V (Å^3)	470.27 (2)	472.88 (3)	476.23 (3)	479.16 (3)	482.48 (3)	485.98 (3)
Z	2					
Radiation type	Mo *Kα*					
μ (mm^{-1})	11,79	11,73	11,65	11,58	11,5	11,41
Crystal size (mm)	0.3×0.2×0.2					
Data collection						
Diffractometer	XtaLAB Synergy, Single source at home/near, HyPix					
Absorption correction	*Multi-scan CrysAlis PRO* 1.171.41.104a (Rigaku Oxford Diffraction, 2021) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.					
T_{min}, T_{max}	0.463, 1	0.386, 1	0.464, 1	0.422, 1	0.419, 1	0.492, 1
No. of measured, independent and observed [I > 3σ(I)] reflections	5321, 982, 980	2511, 847, 837	2431, 894, 884	2805, 903, 891	2907, 950, 936	2753, 945, 931
R_{int}	0,053	0,023	0,019	0,024	0,024	0,023
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0,678	0,696	0,687	0,721	0,723	0,724
Refinement						
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.038, 0.046, 3.54	0.018, 0.023, 1.44	0.017, 0.022, 1.35	0.019, 0.024, 1.48	0.019, 0.024, 1.43	0.020, 0.024, 1.41
No. of reflections	982	847	894	903	950	945
No. of parameters	82	82	82	82	82	82

2	Absolute structure, Friedel pairs used in the refinement	427	283	327	327	373	365

Table S9. Change in bond lengths (Å) of $Nd(Ca_{0.8}Sr_{0.2})_4O(BO_3)_3$ in the temperature range 273-1273 K.

T, K	300	473	673	873	1073	1273
*M*1—O1^{ii}	2.269 (11)	2.270 (7)	2.270 (7)	2.279 (7)	2.280 (7)	2.283 (7)
*M*1—O1^{i}	2.291 (9)	2.303 (6)	2.302 (6)	2.307 (6)	2.310 (6)	2.314 (6)
*M*1—O6^{v}	2.438 (11)	2.445 (7)	2.448 (7)	2.451 (8)	2.464 (8)	2.468 (8)
*M*1—O4	2.440 (7)	2.450 (4)	2.458 (4)	2.461 (4)	2.462 (4)	2.467 (5)
*M*1—O4^{iv}	2.440 (7)	2.450 (4)	2.458 (4)	2.461 (4)	2.462 (4)	2.467 (5)
*M*1—O6	2.515 (9)	2.531 (6)	2.542 (6)	2.547 (6)	2.570 (7)	2.587 (7)
<*M*1-O>$_6$	2.399	2.408	2.413	2.418	2.425	2.431
*M*2—O1^{vi}	2.342 (6)	2.340 (4)	2.351 (4)	2.352 (4)	2.358 (4)	2.366 (4)
*M*2—O3^{ix}	2.363 (7)	2.372 (4)	2.380 (4)	2.386 (4)	2.384 (4)	2.397 (4)
*M*2—O5^{ii}	2.372 (7)	2.384 (4)	2.383 (4)	2.397 (4)	2.404 (4)	2.409 (5)
*M*2—O2^{vi}	2.392 (8)	2.386 (5)	2.398 (5)	2.405 (5)	2.410 (5)	2.416 (5)
*M*2—O2^{vii}	2.367 (6)	2.392 (4)	2.407 (4)	2.408 (4)	2.413 (4)	2.434 (5)
*M*2—O3^{viii}	2.409 (8)	2.398 (5)	2.412 (5)	2.411 (5)	2.416 (5)	2.430 (5)
<*M*2-O>$_6$	2.374	2.379	2.389	2.393	2.398	2.409
*M*3—O4	2.357 (7)	2.356 (4)	2.355 (4)	2.361 (4)	2.362 (4)	2.369 (5)
*M*3—O4^{x}	2.370 (8)	2.366 (5)	2.377 (5)	2.381 (5)	2.394 (5)	2.396 (5)
*M*3—O2^{iv}	2.393 (7)	2.400 (4)	2.399 (4)	2.409 (4)	2.422 (4)	2.420 (5)
*M*3—O5^{ix}	2.529 (8)	2.534 (5)	2.553 (5)	2.562 (5)	2.579 (5)	2.586 (6)
*M*3—O3^{ix}	2.547 (7)	2.567 (4)	2.568 (4)	2.584 (5)	2.599 (4)	2.601 (5)
*M*3—O5^{xi}	2.651 (6)	2.665 (4)	2.671 (4)	2.674 (4)	2.679 (4)	2.682 (5)
*M*3—O5^{ii}	2.898 (7)	2.899 (4)	2.905 (4)	2.915 (4)	2.920 (4)	2.934 (5)
*M*3—O6	2.9521 (18)	2.9508 (12)	2.9509 (12)	2.9517 (13)	2.9507 (12)	2.9497 (13)
<*M*3-O>$_8$	2.587	2.592	2.597	2.605	2.613	2.617
B1—O2	1.384 (10)	1.373 (6)	1.372 (6)	1.370 (6)	1.371 (6)	1.369 (6)
B1—O2^{iv}	1.384 (10)	1.373 (6)	1.372 (6)	1.370 (6)	1.371 (6)	1.369 (6)
B1—O6	1.365 (18)	1.373 (11)	1.373 (10)	1.388 (10)	1.378 (10)	1.375 (11)
<B1-O>$_3$	1.378	1.373	1.372	1.376	1.373	1.371
B2—O3^{v}	1.372 (11)	1.363 (7)	1.354 (7)	1.364 (7)	1.367 (7)	1.357 (7)
B2—O5	1.393 (12)	1.382 (8)	1.384 (7)	1.381 (7)	1.379 (7)	1.380 (8)
B2—O4^{xii}	1.374 (12)	1.397 (8)	1.399 (8)	1.387 (8)	1.390 (8)	1.398 (8)
<B2-O>$_3$	1.380	1.381	1.379	1.377	1.379	1.378

Table S10. Coefficients of approximation of temperature dependencies by polynomial function ($p_T = p_0 + p_1T + p_2T^2$) of $(Ca_{1-x}Sr_x)_4NdO(BO_3)_3$ (x = 0, 0.2, 0.5) solid solutions.

	p_0	$p_1\times10^3$	$p_2\times10^6$
		$Ca_4NdO(BO_3)_3$ (x = 0)	
a	8.125426(57)	0.07513(31)	0.01476(36)
b	16.04469(21)	0.1070(11)	0.0352(13)
c	3.590466(24)	0.04180(13)	0.00967(15)
β	101.36470(54)	0.0798(30)	0.101(35)
V	458.9131(78)	12.492(43)	3.093(51)
		$(Ca_{1.8}Sr_{0.2})_4NdO(BO_3)_3$ (x = 0.2)	
a	8.16505(26)	0.0000851(15)	0.0018(17)
b	16.14137(65)	0.0001051(36)	0.0293(43)
c	3.614363(83)	0.00004589(46)	0.00588(54)
β	101.4574(12)	0.0000881(69)	0.1158(83)
V	467.18(32)	12.0(19)	3.2(23)
		$(Ca_{0.5}Sr_{0.5})_4NdO(BO_3)_3$ (x = 0.2)	
a	8.27112(49)	0.0861(27)	0.0048(31)
b	16.33471(70)	0.1132(38)	0.0091(45)
c	3.67570(25)	0.0453(13)	0.0071(15)
β	101.6636(33)	0.093(18)	0.075(21)
V	486.351(70)	14.29(39)	0.91(45)