Electronic Supplementary Material (ESI) for Dalton Transactions.

Unprecedented rock-salt ordering of A and B cations in the double perovskite $Nd_{2-x}Ca_xMgTiO_{6-d}$ and defect association

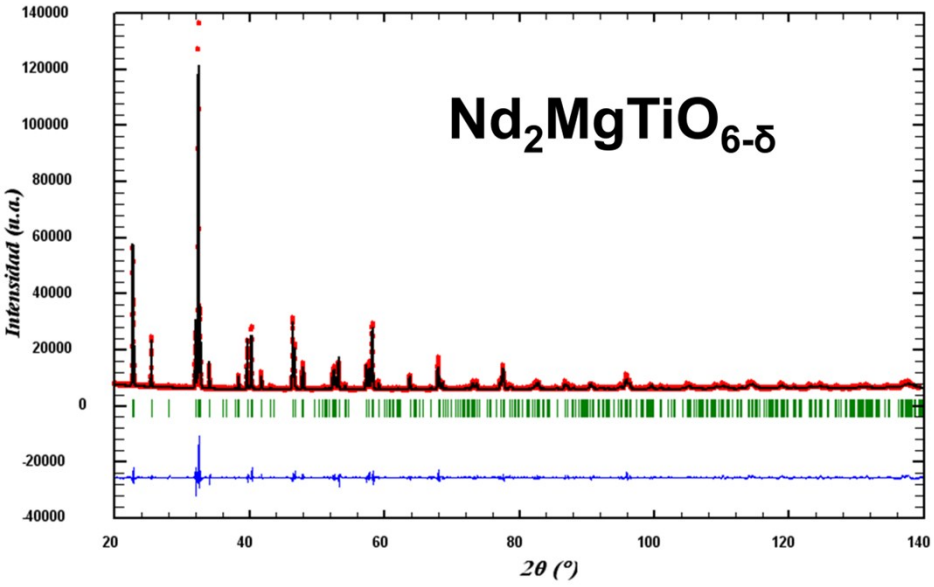
M. Teresa Azcondo,[a,*] Khalid Boulahya,[b] Clemens Ritter,[c] Flaviano García-Alvarado[a] and Ulises Amador[a]

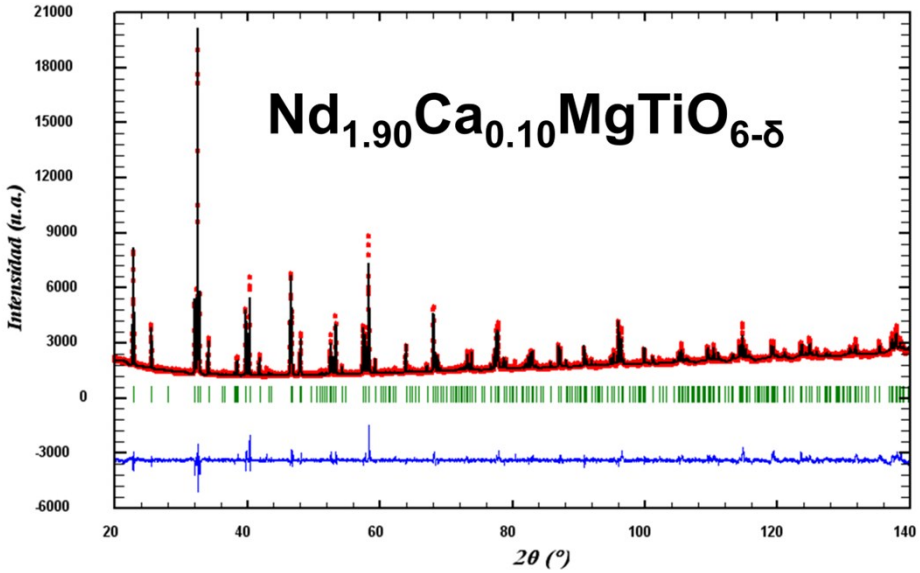
[a] Universidad San Pablo-CEU, CEU Universities, Facultad de Farmacia, Departamento de Química y Bioquímica, Urbanización Montepríncipe, Boadilla del Monte, E-28668, Madrid, Spain.

[b] Departamento de Química Inorgánica, Facultad de Química, Universidad Complutense, E-28040 Madrid, Spain.

[c] Institut Laue-Langevin, BP 156-38042 Grenoble Cedex 9, France.

* e-mail: azcondo@ceu.es
Phone: (34) 91 372 47 15
Fax: (34) 91 351 04 96.





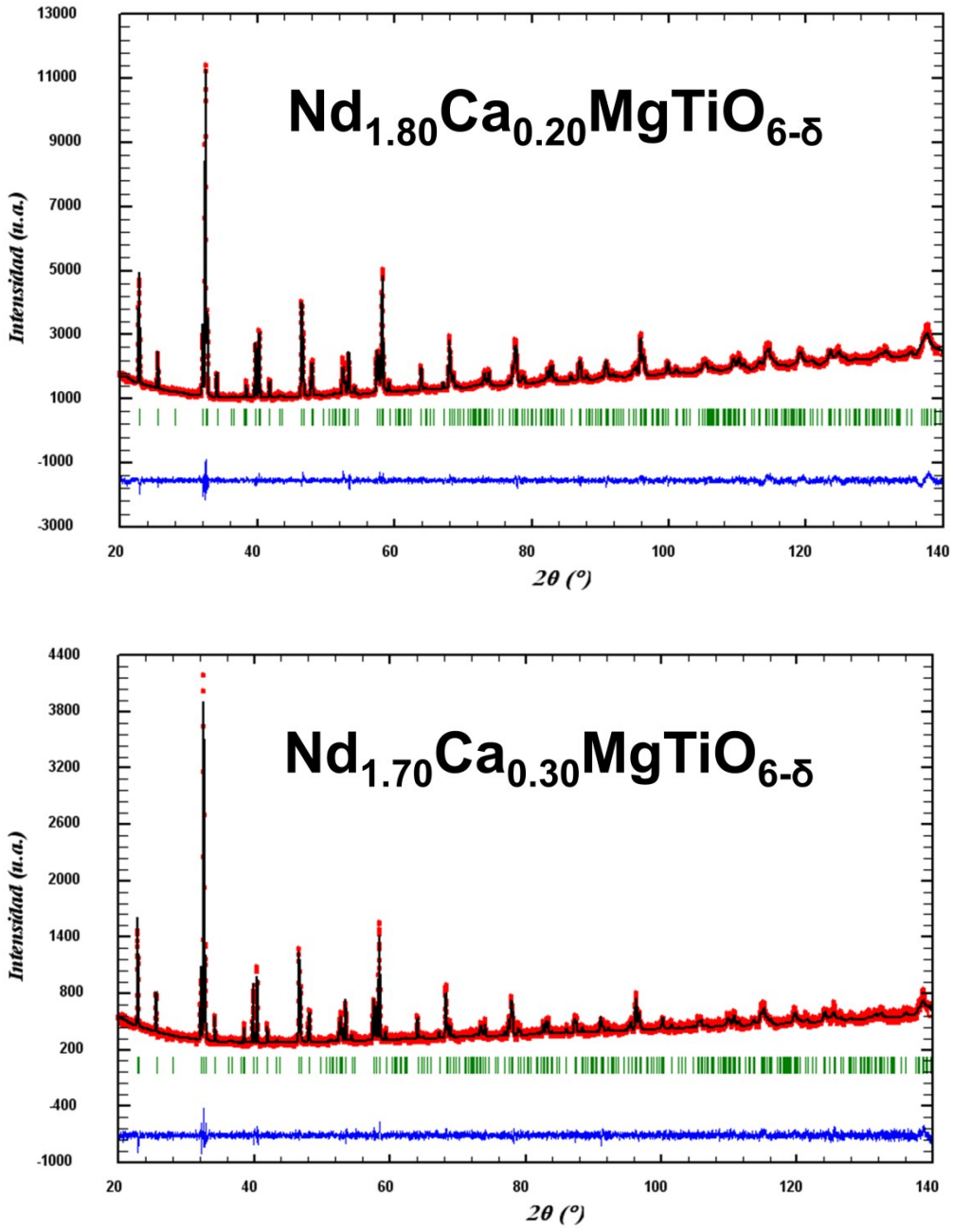


Figure SI 1. Experimental (red circles) and calculated (black continuous line) XRD patterns (and their difference, blue line at the bottom) for samples of the series $Nd_{2-x}Ca_xMgTiO_{6-\delta}$ with (x= 0, 0.10, 0.20 and 0.30) prepared in air. Vertical bars indicate the positions of the Bragg peaks of the identified phases contained in the sample.

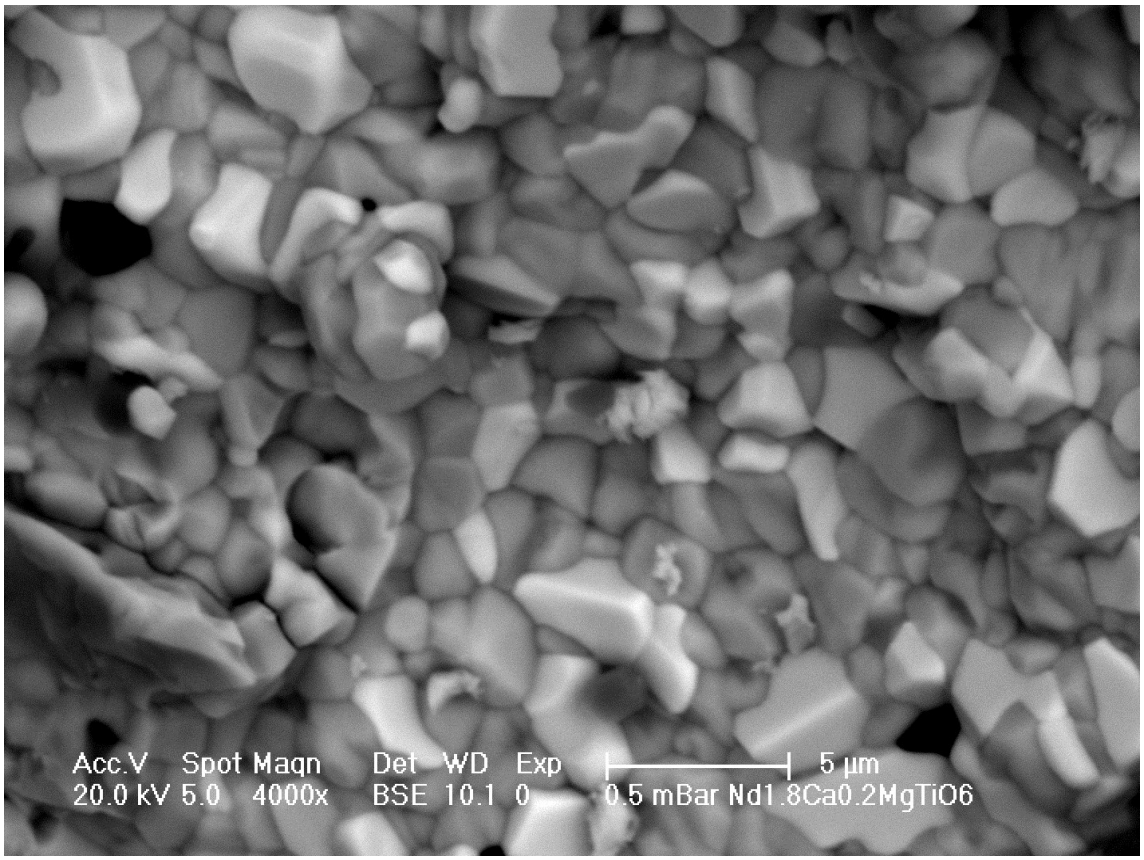


Figure SI 2: Back-scattered electrons (BSE) image taken at a magnification of x 4000 on a sample of composition $Nd_{1.80}Ca_{0.20}MgTiO_{6-\delta}$. Segregation of two different phases is evident as revealed by their different contrasts.

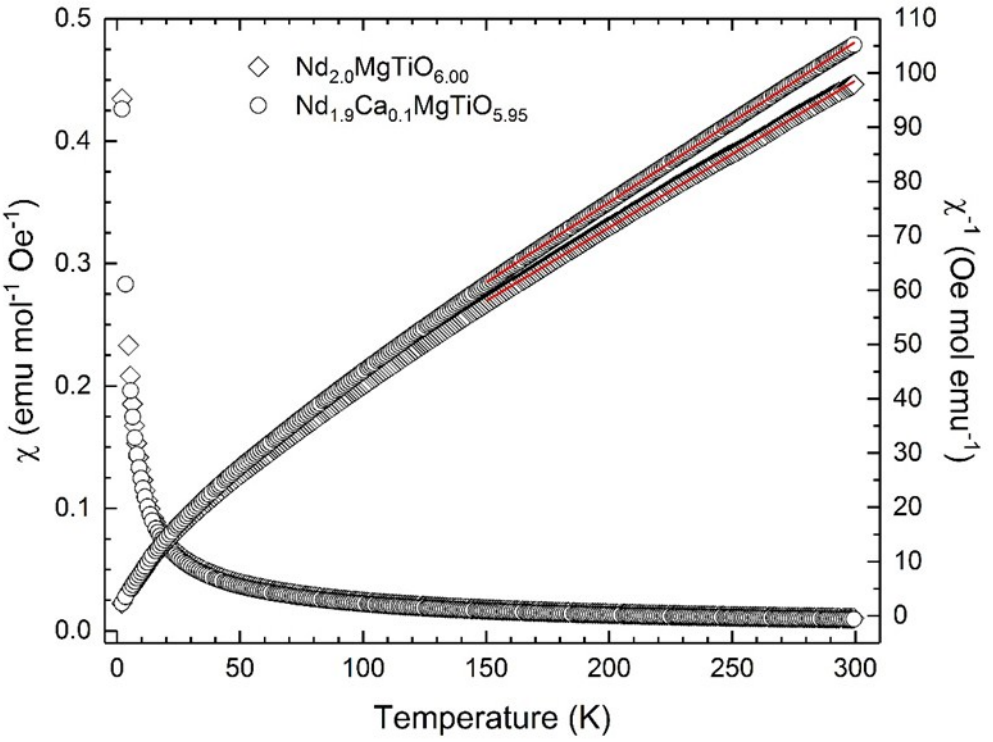


Figure SI 3. Temperature dependence, in an applied magnetic field of 100 mT, of the molar magnetic susceptibility and its inverse for Nd_2MgTiO_6 (circles) and $Nd_{1.9}Ca_{0.1}MgTiO_{5.95}$ (diamonds) compounds. The solid red lines correspond to the fits of χ^{-1} data from RT tp 150 K to the inverse of the Curie-Weiss law.

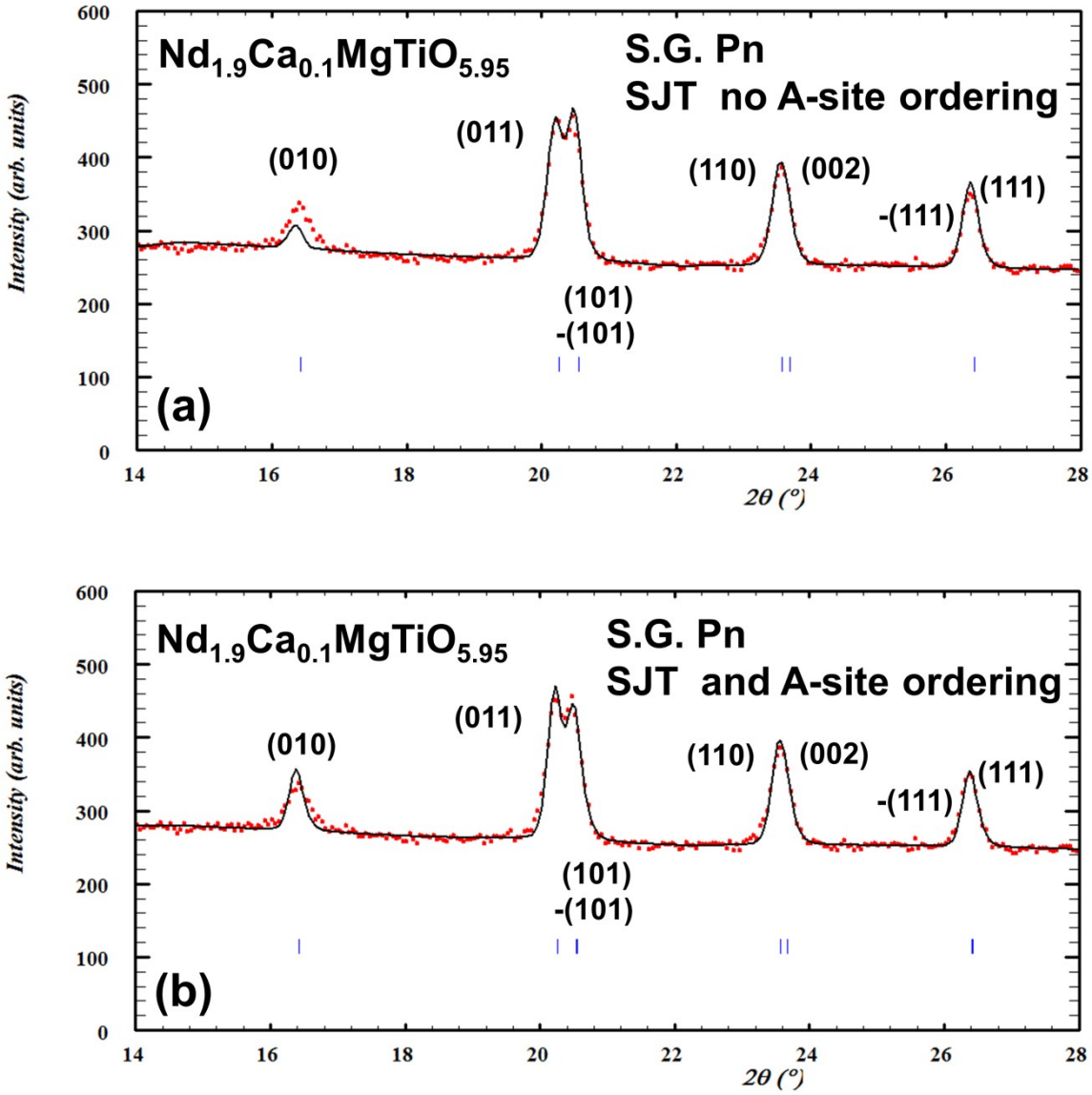


Figure SI 4. Enlargement of the low-angle zone of the NPD data of $Nd_{1.9}Ca_{0.1}MgTiO_{5.95}$ fitted to a structural model with Pn S.G. due to the loss of symmetry (from $P2_1/n$ to Pn) associated to (a) only the second-order Jahn-Teller effect (SJT) due to tetravalent titanium and (b) the combined effect of SJT and rock-salt ordering of A-ions. Note that the intensity of the (010) Bragg peak, forbidden in the S.G. $P2_1/n$ of the parent (un-doped) material, is much better accounted for with the latter model.

Table SI 1. Nominal and experimental (determined by EDS) compositions for the $Nd_2MgTiO_{6-\delta}$ sample used for NPD and electrical characterization.

Element	Nominal composition (atom %)	Experimental composition (atom %)
Nd	20.0	20.6(3)
Mg	10.0	10.3(2)
Ti	10.0	9.5(3)
O	60.0	59.6(3)

Table SI 2. Nominal and experimental (determined by EDS) compositions for the $Nd_{1.90}Ca_{0.10}MgTiO_{6-\delta}$ sample used for NPD and electrical characterization.

Element	Nominal composition (atom %)	Experimental composition (atom %)
Nd	19.0	19.2(4)
Ca	1.0	1.0(1)
Mg	10.0	10.8(1)
Ti	10.0	10.4(1)
O	60.0	58.6(4)

Table SI 3. Structural parameters for $Nd_{2-x}Ca_xMgTiO_{6-\delta}$ obtained from joint fitting of NPD and XRD data. Agreement factors are given for the fitting of NPD data.

Sample	**x= 0.00** [a]			**x = 0.10** [b]		
Space Group	$P2_1/n$		**Space Group**	Pn		
***a* (Å)**	5.4599(1)		***a* (Å)**	5.4621(1)		
***b* (Å)**	5.5871(1)		***b* (Å)**	5.5791(1)		
c (Å)	7.7681(1)		**c (Å)**	7.7689(2)		
β (deg)	90.005(1)		**β (deg)**	90.003(4)		
Volume (Å^3)	236.97(1)		**Volume (Å^3)**	236.75(1)		
A position	4e	**O1 position**	4e	**A´ position**	2a	**O1b position**	2a
Occ Nd	1	**X**	0.3015(5)	**Occ Nd/Ca**	0.90(1)/0.10(1)	**X**	0.786(4)
X	0.0097(3)	**Y**	0.2872(4)	**X**	0.084(4)	**Y**	0.972(1)
Y	0.0473(2)	**Z**	0.9528(4)	**Y**	0.290(6)	**Z**	0.141 (4)
Z	0.7509(3)	**Occ**	1.000(4)	**Z**	0.841(4)	**Occ**	1.002(3)
U*100 (Å^2)	0.03(1)	**U*100 (Å^2)**	0.17(2)	**U*100 (Å^2)**	0.45(7)	**U*100 (Å^2)**	0.29(4)
B' position	2c	**O2 position**	4e	**A" position**	2a	**O2a position**	2a
Occ Mg	1	**X**	0.2872(5)	**Occ Nd/Ca**	1.00(1)/0	**X**	0.366(4)
U*100 (Å^2)	0.55(4)	**Y**	0.3035(4)	**X**	0.067(4)	**Y**	0.553(2)
B" position	2d	**Z**	0.5446(4)	**Y**	0.1958(6)	**Z**	0.636(4)
Occ Ti	1	**Occ**	0.998(3)	**Z**	0.340(4)	**Occ**	1.000(2)
U*100 (Å^2)	0.58(4)	**U*100 (Å^2)**	0.17(2)	**U*100 (Å^2)**	0.06(4)	**U*100 (Å^2)**	0.29(4)
		O3 position	4e	**B´ position**	2a	**O2b position**	2a
		X	0.9126(3)	**Occ Mg/Ti**	0.127(3)/0.873(3)	**X**	0.787(4)
		Y	0.4763(3)	**X**	0.59047	**Y**	0.956(1)
		Z	0.7429(4)	**Y**	0.262(3)	**Z**	0.546(4)
		Occ	1.002(4)	**Z**	0.09002	**Occ**	0.998(4)
		U*100 (Å^2)	0.17(2)	**U*100 (Å^2)**	0.01(3)	**U*100 (Å^2)**	0.29(4)
				B" position	2a	**O3a position**	2a
				Occ Mg/Ti	0.873(3)/0.127(3)	**X**	-0.007(4)
				X	0.0912(3)	**Y**	0.736(1)
				Y	0.764(2)	**Z**	0.833(4)
				Z	0.082(3)	**Occ**	0.999(3)
				U*100 (Å^2)	0.01(4)	**U*100 (Å^2)**	0.29(4)
				O1a position	2a	**O3b position**	2a
				X	0.387(4)	**X**	0.164(4)
				Y	0.555(2)	**Y**	0.782(1)
				Z	0.045(4)	**Z**	0.344(4)
				Occ	0.945(5)	**Occ**	1.003(3)
				U*100 (Å^2)	0.29(4)	**U*100 (Å^2)**	0.29(4)
[a] $P2_1/n$ (#14): 4e (xyz), 2c (½ 0 ½), 2d (½ 0 0), χ^2= 1.94, R_{wp}= 4.31%, R_{exp}= 3.10%, R_B= 2.69%, Composition: $Nd_2MgTiO_{6.00(1)}$				[b] Pn (#7): 2a (xyz) χ^2= 11.0, R_{wp}= 3.69%, R_{exp}= 1.11%, R_B= 2.81%, Composition: $Nd_{1.90(1)}Ca0_{.10(1)}MgTiO_{5.94(1)}$			

Table SI 4. Selected structural information for $Nd_{2-x}Ca_xMgTiO_{6-\delta}$ (x=0.00, 0.10) obtained from NPD data. Angles are given in degrees and distances in Å (up to 3.50 Å); distortion Δ of the BO_n polyhedra and Bond Valence Sums [1], are reported as $\Delta=1/n\ \Sigma_{j=1,n}\ \{(d_n - <d>)/<d>\}^2$ where <d> is the average B-O distance. The quadratic elongation λ is given by $\lambda= \Sigma_{j=1,n}\ (l_i/l_0)^2/n$ and the bond-angle variance σ is given by $\sigma = \Sigma_{j=1,n}\ (\theta_i- \theta_0)^2/(n-1)$ where l_0 and θ_0 are the cation-anion bond lengths and cation-anion-cation bond angles in regular coordination polyhedra, respectively, and l_i and θ_i are the cation-anion bond lengths and cation-anion-cation bond angles of the ith bond [2]

$Nd_2MgTiO_{6.00(1)}$		**$Nd_{1.90(1)}Ca_{0.10(1)}MgTiO_{5.94(1)}$**			
[a] Tilt angle θ	20.05(3)/19.77(4)	**[a] Tilt angle θ**	21.0(1)/17.6(2)		
[b] Tilt angle φ	20.05(3)/19.77(4)	**[b] Tilt angle φ**	21.0(1)/17.7(1)		
[c] Tilt angle μ	14.5(1)/14.2(1)	**[c] Tilt angle μ**	15.8(3)/12.5(3)		
TiO_6 octahedron		**B´(Mg/Ti)O_6 octahedron**			
B'-O(1) x 2	1.970(2)	**B'-O1a x 1**	2.01(2)		
B'-O(2) x 2	1.945(3)	**B'-O1b x 1**	1.98(1)		
B'-O(3) x 2	1.951(3)	**B'-O2a x 1**	1.86(2)		
		B'-O2b x 1	2.08(2)		
		B'-O3a x 1	1.96(3)		
		B'-O3b x 1	1.97(3)		
Average B'-O	1.956(1)	**Average B'-O**	1.98(1)		
Octahedron volume (Å³)	9.966	**Octahedron volume (Å³)**	10.262		
Distortion B'-O_6 x 10^4	0.30	**Distortion B'-O_6 x 10^4**	11.2		
Quadratic elongation	1.0003	**Quadratic elongation**	1.0031		
Bond angle variance	0.6761 deg²	**Bond angle variance**	6.7651 deg²		
BVS	4.11(1)	**BVS**	3.91(8)		
MgO_6 octahedron		**B''(Mg/Ti)O_6 octahedron**			
B''-O(1) x 2	2.064(3)	**B''-O1a x 1**	2.01(2)		
B''-O(2) x 2	2.085(3)	**B''-O1b x 1**	2.08(2)		
B''-O(3) x 2	2.058(3)	**B''-O2a x 1**	2.19(2)		
		B''-O2b x 1	1.92(2)		
		B''-O3a x 1	2.01(4)		
		B''-O3b x 1	2.08(4)		
Average B''-O	2.069(1)	**Average B''-O**	2.05(1)		
Octahedron volume (Å³)	11.7966	**Octahedron volume (Å³)**	11.4448		
Distortion B'-O_6 x 10^4	0.31	**Distortion B''-O_6 x 10^4**	17.0		
Quadratic elongation	1.0004	**Quadratic elongation**	1.0035		
Bond angle variance	1.2459 deg²	**Bond angle variance**	6.2738 deg²		
BVS	2.18(1)	**BVS**	2.33(7)		
NdO_n polyhedron		**(Nd/Ca)O_n polyhedron**		**NdO_n polyhedron**	
Nd-O1 x 1	2.606(3)	**(Nd/Ca)-O1a x 1**	2.73(2)	**Nd-O1a x 1**	2.33(3)
Nd-O1 x 1	2.383(3)	**(Nd/Ca)-O1a x 1**	2.68(4)	**Nd-O1b x 1**	2.51(3)
Nd-O1 x 1	2.740(4)	**(Nd/Ca)-O1b x 1**	2.40(3)	**Nd-O2a x 1**	2.38(3)
Nd-O2 x 1	2.629(3)	**(Nd/Ca)-O2a x 1**	2.66(3)	**Nd-O2b x 1**	2.59(3)
Nd-O2 x 1	2.368(4)	**(Nd/Ca)-O2a x 1**	2.73(4)	**Nd-O2b x 1**	2.72(4)
Nd-O2 x 1	2.716(4)	**(Nd/Ca)-O2b x 1**	2.38(3)	**Nd-O3a x 1**	2.36(3)
Nd-O3 x 1	2.456(2)	**(Nd/Ca)-O3a x 1**	2.54(1)	**Nd-O3b x 1**	2.37(3)
Nd-O3 x 1	2.341(2)	**(Nd/Ca)-O3b x 1**	2.33(3)		
Average Nd-O	2.530(1)	**Average (Nd/Ca)-O**	2.55(1)	**Average Nd-O**	2.47(1)
BVS	2.75(1)	**BVS**	2.57(8)	**BVS**	2.77(9)
[a] With [110], [b] With [1-10], [c]With [001]					

[1] Zachariasen, W.H., Acta Crystallographica, 1963. **16**: p. 385.
[2] Robinson, K., Gibbs, G. V. & Ribbe, P. H., Science, 1971. **172**: p. 567-570.

Table SI 5. Curie constant C and Weiss temperature θ values obtained by fitting the inverse of the molar magnetic susceptibility data to the function $\chi^{-1} = (\frac{C}{T-\theta})^{-1}$ in the temperature range 150–300 K; and the experimental magnetic moment μ_{exp} values calculated as $\sqrt{8 \times \frac{C}{2-x}}$

Compound ($Nd_{2-x}Ca_xMgTiO_{6-\delta}$)	C (emu K mol^{-1} Oe^{-1})	θ (K)	μ_{exp} (μ_B per Nd)
Nd_2MgTiO_6 (x=0.00)	3.384±0.004	-64.5±0.5	3.68±0.04
$Nd_{1.90}Ca_{0.10}MgTiO_{5.95}$ (x=0.10)	3.331±0.002	-57.7±0.2	3.65±0.03