



# CaFeFeNbO<sub>6</sub> – an iron-based double double perovskite†‡

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**Ordering of cations is important for controlling properties of ABO<sub>3</sub> perovskites, and CaFeFeNbO<sub>6</sub> is the first example of an Fe-based AA'BB'O<sub>6</sub> double double perovskite, with Ca<sup>2+</sup>/Fe<sup>2+</sup> ordered on A-site columns, and Fe<sup>3+</sup>/Nb<sup>5+</sup> at the octahedral B-sites. Substantial (37%) antisite disorder of the latter cations leads to spin glassy magnetism below a freezing transition at 12 K. The CaMnFeNbO<sub>6</sub> analogue also shows substantial cation disorder and spin glassy behaviour. Comparison of synthesis pressures for ordered materials based on different A-site transition metals, suggests that pressures of at least 14–18 GPa will be required to discover the expected plethora of double double perovskites based on A' cations smaller than Mn<sup>2+</sup>.**

Cation ordering within ABO<sub>3</sub> perovskite oxides generates new structures and emergent physical properties,<sup>1</sup> most famously in B-cation ordered A<sub>2</sub>BB'O<sub>6</sub> double perovskites where rock-salt ordering of B/B' transition metal cations<sup>2–4</sup> leads to ferrimagnetism and large magnetoresistance in Sr<sub>2</sub>FeMoO<sub>6</sub> and related materials.<sup>5,6</sup> A variety of AA'B<sub>2</sub>O<sub>6</sub> double perovskites based on columnar A-cation ordering has also been discovered through high pressure synthesis. This was first reported in CaFeTi<sub>2</sub>O<sub>6</sub>, synthesised at 12–15 GPa,<sup>7</sup> and several series based on A-site ordering of rare-earth (R) and Mn cations with the same P<sub>4</sub>/nmc double perovskite structure; e.g. RMn(Ga<sub>0.5</sub>Ti<sub>0.5</sub>)<sub>2</sub>O<sub>6</sub> and RMn(Mn,Ti)<sub>2</sub>O<sub>6</sub>, have subsequently been reported from syntheses at lower pressure (6 GPa).<sup>8–11</sup> CaMnTi<sub>2</sub>O<sub>6</sub> and CaMn(Ti,V)<sub>2</sub>O<sub>6</sub> derivatives have a symmetry-lowered P<sub>4</sub>mc double perovskite structure where loss of an inversion centre gives rise to ferroelectricity.<sup>12,13</sup> Combining the columnar A-site order with

1:1 order of B-cations gives rise to AA'BB'O<sub>6</sub> double double perovskites. RMn<sub>3</sub>O<sub>6</sub> (NaNbO<sub>3</sub>-type, *Pmmn*) materials have columnar R/Mn A-site and layered Mn charge-ordering at the B-sites,<sup>14</sup> but double perovskites based on orders of different metals have a tetragonal P<sub>4</sub>/n structure with columnar A/A' and rocksalt type B/B' orders.

Many P<sub>4</sub>/n AA'BB'O<sub>6</sub> double double perovskites with A' = Mn have been synthesised at 10 GPa; RMnMnB'O<sub>6</sub> (B' = Sb<sup>15,16</sup> and Ta<sup>17</sup>) and CaMnBB'O<sub>6</sub> (B = Mn, Fe, Co, Ni for B' = Re,<sup>18–20</sup> and B/B' = Fe/Ta,<sup>21</sup> Cr/Sb, Fe/Sb<sup>22</sup> and Mn/W<sup>23</sup>); and recently the first non-Mn analogue CaCuFeReO<sub>6</sub> was made at 15.5 GPa.<sup>24</sup> The CaA'FeReO<sub>6</sub> (A' = Mn, Mn<sub>0.5</sub>Cu<sub>0.5</sub>, Cu) materials are notable as ferrimagnets with Curie temperatures above 500 K and varying magnetoresistance properties.<sup>18,24</sup> Recovery of CaCuFeReO<sub>6</sub> from 15.5 GPa suggests that many further AA'BB'O<sub>6</sub> double double perovskites based on other A' metals may be accessible at pressures above 10 GPa. A' = Fe is a likely possibility given the columnar cation ordering in double perovskite CaFeTi<sub>2</sub>O<sub>6</sub>. A-site Fe<sup>2+</sup> perovskites are of interest given the predominance of (Mg, Fe)SiO<sub>3</sub> perovskite in earth's lower mantle, and may have notable magnetic properties such as the unusual multiple-sublattice Fe<sup>2+</sup> spin order recently reported in CaFe<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub>,<sup>25</sup> which has 1Ca<sup>2+</sup>:3Fe<sup>2+</sup> A-site order, but such recovered materials are rare. We report here high pressure exploration of CaFeFeNbO<sub>6</sub> and the Mn-comparator CaMnFeNbO<sub>6</sub>, leading to the discovery that both form P<sub>4</sub>/n double double perovskites although with significant B-cation disorder leading to spin-glass ground states.

Samples of ideal composition CaMFeNbO<sub>6</sub> (M = Mn, Fe) were treated under high pressure and high temperature conditions in a Walker-type multianvil press. The precursor mixture comprised stoichiometric amounts of Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub> (obtained by heating a pellet of CaCO<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> at 1200 °C for 24 h under an N<sub>2</sub> flow), MO (M = Mn, Fe) and Nb<sub>2</sub>O<sub>5</sub>. The mixture was packed into a Pt capsule, compressed to the synthesis pressure, heated over 10 minutes to the synthesis temperature, held at this temperature for 30 minutes, quenched to room temperature, and decompressed to ambient pressure. For M = Mn,

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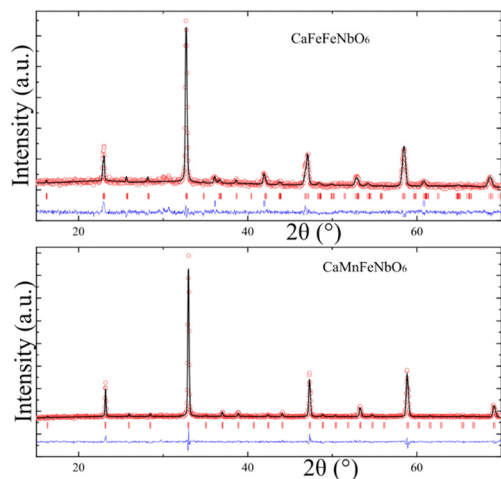
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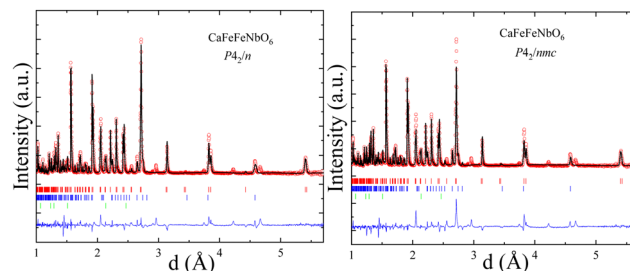


**Fig. 1** Rietveld fits to room temperature PXD patterns of  $\text{CaMnFeNbO}_6$  ( $M = \text{Mn, Fe}$ ) samples. A  $P4_2/n$  double double perovskite model is fitted in both cases, although PXD does not discriminate well between possible superstructures. Lower Bragg markers for  $M = \text{Fe}$  are for  $\text{FeO}$  impurity.

reactions were performed at 10–12 GPa and 1000–1200 °C, and the optimum synthesis conditions were found to be 10 GPa and 1200 °C. Reactions were performed at 10–14 GPa and 1000–1400 °C for  $M = \text{Fe}$ , and the optimum synthesis conditions were found to be 14 GPa and 1400 °C. Laboratory powder X-ray diffraction (PXD) patterns were collected using a D2 Bruker diffractometer and powder neutron diffraction (PND) data were measured at the WISH beamline of the ISIS facility,<sup>26</sup> and on diffractometer D20 at ILL. Magnetization was measured using an MPMS SQUID magnetometer.

Powder X-ray diffraction showed that both  $\text{CaMnFeNbO}_6$  ( $M = \text{Mn, Fe}$ ) compositions form a majority perovskite-structured phase at the optimum conditions above. However, secondary phases were present and were not eliminated in repeated syntheses. Fits to the PXD data (Fig. 1) demonstrate that both products are consistent with the  $P4_2/n$  double double perovskite structure, although X-ray scattering does not discriminate well between different superstructure models and PND refinements were used to resolve these issues. Further results for  $\text{CaMnFeNbO}_6$  are shown in ESI† Fig. S1–S7.

Fits to high resolution time-of-flight PND data for the  $\text{CaFeFeNbO}_6$  sample show that the main phase is a cation-ordered perovskite, but  $\text{CaFeO}_{3-x}$  perovskite,  $\text{FeO}$  and unidentified impurity are also observed. A-cation occupancies were varied in initial refinements but no disorder or off-stoichiometry was found, in keeping with the very different respective coordination numbers of 10 and 4 at Ca and Fe sites. The PND data do not show a clear superstructure peak from Fe/Nb B-site ordering (expected at  $d = 4.4$  Å), so refinements of  $P4_2/nmc$  double perovskite ( $\text{CaFe}(\text{Fe}_{0.5}\text{Nb}_{0.5})_2\text{O}_6$  where B-cations are fully disordered) and  $P4_2/n$  double double perovskite ( $\text{CaFeFeNbO}_6$  with partial or full Fe/Nb order) models were compared, making use of the good Fe/Nb neutron contrast ( $b = 9.54/7.05$  fm), as shown in Fig. 2. Comparison of the fits by eye and through their residuals shows that the double double perovskite model gives a



**Fig. 2** Comparison of Rietveld fits to PND data for  $\text{CaFeFeNbO}_6$  collected at 300 K using (left) the  $P4_2/n$  double double perovskite (residuals:  $R_p = 4.91\%$ ,  $R_{wp} = 7.22\%$ ,  $R_{Bragg} = 6.28\%$ ,  $R_F = 3.23\%$ , and (right) a  $P4_2/nmc$  double perovskite model ( $R_p = 7.16\%$ ,  $R_{wp} = 10.30\%$ ,  $R_{Bragg} = 14.30\%$ ,  $R_F = 8.37\%$ ). Secondary phase markers are for  $\text{CaFeO}_{3-x}$  (16.2(1)%) and  $\text{FeO}$  (8.2(1)%) and small unidentified impurity peaks are also observed in the difference curve.

substantially better fit, so this is taken to be the best structural description. Refinement results are shown in Table 1 and Fig. 3.

$\text{CaFeFeNbO}_6$  is confirmed as having the  $P4_2/n$  double double perovskite structure, and so is the first reported Fe-based material in this family. Results in Table 1 show a substantial (37%) Fe/Nb antisite disorder at the B-sites. A similar (34%) antisite disorder was reported in the double perovskite  $\text{Ca}_2\text{FeNbO}_6$ ,<sup>27</sup> and no long range Fe/Nb cation order was found in a recent neutron diffraction study of  $\text{Sr}_2\text{FeNbO}_6$ .<sup>28</sup> Disorder between  $\text{Fe}^{3+}$  and  $\text{Nb}^{5+}$  accounts for the lack of a clear superstructure peak at  $d = 4.4$  Å for  $\text{CaFeFeNbO}_6$ , and likely reflects their similar ionic radii (0.645 and 0.64 Å respectively) and a formal charge difference of only 2. Synthesis at higher pressure or lower temperature might reduce the disorder. Despite their similar radii, the average B1–O = 1.97 Å distance for the Nb-rich site is smaller than B2–O = 2.05 Å for the Fe-rich site. This may reflect disordered off-centre second-order Jahn–Teller distortions for  $d^0$   $\text{Nb}^{5+}$  that reduce the crystallographic average

**Table 1** Crystal structure parameters for  $\text{CaFeFeNbO}_6$  from the 300 K  $P4_2/n$  neutron Rietveld fit with derived bond distances (Å) below. Cell parameters are  $a = 7.6485(1)$  and  $c = 7.7145(2)$  Å. Residuals are shown in the Fig. 2 caption

Atom, Wyckoff site	x	y	z	$B_{iso}$ (Å <sup>2</sup> )	Occ
Ca, 4e	0.2500	0.7500	0.7791(1)	1.5(2)	1
A1(Fe), 2a	0.7500	0.7500	0.7500	1.6(1)	1
A2(Fe), 2b	0.2500	0.2500	0.7500	1.6	1
B1(Fe/Nb), 4c	0.0000	0.5000	0.5000	1.6	0.37(3)/0.63
B2(Fe/Nb), 4d	0.0000	0.0000	0.5000	1.6	0.63/0.37
O1, 8g	−0.065(1)	0.548(1)	0.243(1)	1.4(1)	1
O2, 8g	−0.248(2)	−0.043(1)	0.575(1)	1.4	1
O3, 8g	−0.227(1)	0.059(1)	−0.039(1)	1.4	1
Ca–O1(x2)	2.685(8)		B1–O1(x2)	2.08(1)	
Ca–O1(x2)	2.877(6)		B1–O2(x2)	2.03(1)	
Ca–O2(x2)	2.508(6)		B1–O3(x2)	1.82(1)	
Ca–O3(x2)	2.486(8)		<B1–O>	1.97(1)	
Ca–O3(x2)	2.359(8)		B2–O1(x2)	1.97(1)	
<Ca–O>	2.583(8)		B2–O2(x2)	2.02(1)	
A1–O2(x4)	2.084(5)		B2–O3(x2)	2.17(1)	
A2–O1(x4)	2.104(8)		<B2–O>	2.05(3)	

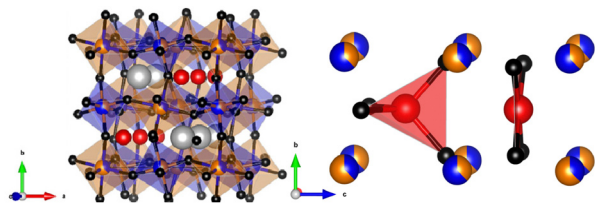


Fig. 3 Crystal structure of the tetragonal  $P4_2/n$  AA'BB'O<sub>6</sub> double double perovskite CaFeFeNbO<sub>6</sub>. A/A'/B/B' sites are grey/red/blue/brown and Fe/Nb disorder is shown within the B/B' octahedra. Detail at the right shows alternating square planar and tetrahedral Fe<sup>2+</sup> coordinations in the A' column.

distance. The average Ca–O distance of 2.58 Å is shorter than the expected value of 2.61 Å from ionic radii, whereas the A-site Fe–O distances of 2.08 and 2.10 Å are longer than expected values of 2.01 and 2.02 Å for tetrahedral and square planar coordinations, respectively. This reveals lattice strain from ordering large Ca<sup>2+</sup> and small Fe<sup>2+</sup> cations in alternate A-site columns of the perovskite framework.

Magnetisation data for the CaFeFeNbO<sub>6</sub> sample are shown in Fig. 4. The susceptibility  $\chi$  in Fig. 4a reveals paramagnetic behaviour, and the effective magnetic moment per CaFeFeNbO<sub>6</sub> unit (calculated as  $\mu_{\text{eff}} = 2.83\sqrt{\chi T}$ ) at high temperatures (>250 K) is close to the theoretical spin-only value of 7.7  $\mu_B$  for high spin Fe<sup>2+</sup> and Fe<sup>3+</sup> cations, hence confirming the mixed Fe-valency in CaFe<sup>2+</sup>Fe<sup>3+</sup>Nb<sup>5+</sup>O<sub>6</sub>. However, the inverse susceptibility plot (shown in ESI,† Fig. S8) does not show a linear (Curie–Weiss) variation over the paramagnetic regime, most likely due to impurity contributions. A broad susceptibility peak is observed at 12 K with divergence of zero-field cooled (ZFC) and field-cooled (FC) susceptibilities. This peak shifts to low temperature as applied field increases (Fig. 4b), and to higher temperature with increasing frequency in ac measurements (Fig. 4c). These

susceptibility variations, and also the slightly non-linear and hysteretic magnetisation-field loop at 5 K (Fig. 4d), are all characteristic of a spin-glass, and further analysis of the ac susceptibility peak shift is shown in ESI,† Fig. S9.

Comparison of variable temperature powder neutron patterns for the CaFeFeNbO<sub>6</sub> sample in Fig. 5 show two peaks that appear on cooling at long- $d$  and so are most likely magnetic in origin. A prominent magnetic intensity appears on the peak at  $d = 4.59$  Å from the CaFeO<sub>3-x</sub> impurity on cooling from 300 to 150 K. The magnetic transition is thus above that of stoichiometric CaFeO<sub>3-x</sub> (120 K)<sup>29</sup> but below that of the O-vacancy ordered brownmillerite CaFeO<sub>2.5</sub> (730 K),<sup>30</sup> consistent with the presence of O-vacancies in this impurity. A weak second peak at  $d = 4.93$  Å arises between 150 and 2 K. This could be associated with the 12 K magnetic transition in CaFeFeNbO<sub>6</sub> but the peak does not index on the  $P4_2/n$  cell or simple supercells. As spin order in previous studied  $P4_2/n$  double double perovskites is usually ferrimagnetic and commensurate with the unit cell, and would give rise to strong magnetic diffraction peaks for high spin Fe<sup>2+</sup> and Fe<sup>3+</sup> cations, it is more likely that the  $d = 4.9$  Å peak is due to spin ordering in an impurity phase.

The magnetisation results discussed above plus the lack of clear magnetic diffraction peaks show that CaFeFeNbO<sub>6</sub> is a spin-glass below freezing temperature  $T_f \approx 12$  K. This can be attributed to the high degree of disorder between magnetic Fe<sup>3+</sup> and non-magnetic Nb<sup>5+</sup> cations over the B-sites. Spin glass ground states were also reported for CaMnFeTaO<sub>6</sub> which has substantial Fe/Ta disorder,<sup>21</sup> and in Sr<sub>2</sub>FeNbO<sub>6</sub><sup>27</sup> and many other cation-disordered double perovskites. The substantial Fe/Nb disorder in CaFeFeNbO<sub>6</sub> also masks potentially interesting magnetic and conducting properties related to Fe<sup>2+</sup>/Fe<sup>3+</sup> charge transfer which could lead to ferromagnetic double exchange as found in magnetite.

Results for the CaMFeNbO<sub>6</sub> (M = Mn) analogue shown in ESI,† are very similar to those for M = Fe. CaMnFeNbO<sub>6</sub> adopts

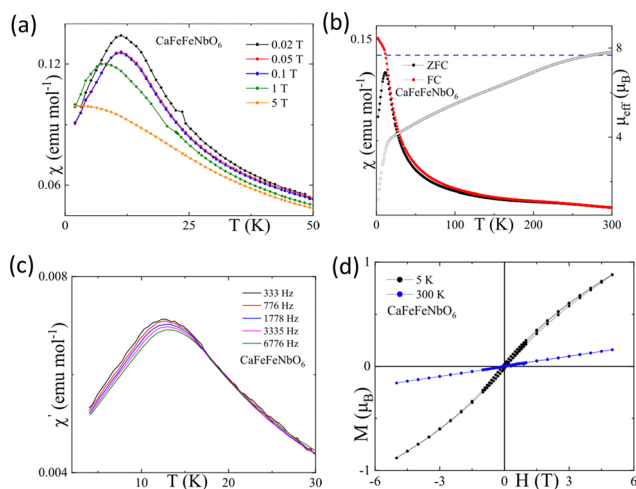


Fig. 4 Magnetic measurements for CaFeFeNbO<sub>6</sub>. (a) ZFC and FC susceptibilities under a 0.1 T field, and the effective moment (calculated from FC susceptibilities) which approximates to the theoretical value of 7.68  $\mu_B$  (blue dashed line) near 300 K. (b) Low temperature ZFC susceptibility under varying fields. (c) Low temperature ac susceptibility at several frequencies. (d) Magnetisation-field loops at 5 and 300 K.

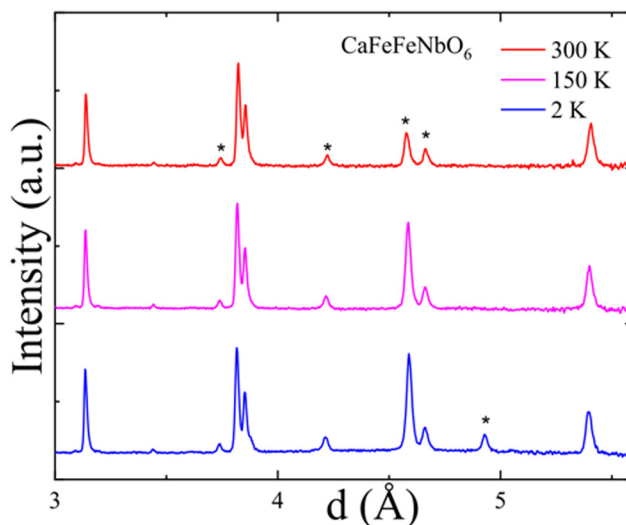


Fig. 5 Comparison of long- $d$  powder neutron patterns for the CaFeFeNbO<sub>6</sub> sample at several temperatures with impurity peaks marked\*.



the  $P4_2/n$  double double perovskite structure with a substantial (29%) Fe/Nb disorder at the B-sites, and also has 16% substitution of Fe for Mn at the A' sites, so the phase has overall stoichiometry  $\text{CaMn}_{0.84}\text{Fe}_{1.16}\text{NbO}_6$ .  $\text{CaMnFeNbO}_6$  shows paramagnetic behaviour at high temperatures and has a magnetic susceptibility peak at 27 K that shifts to higher temperature with increasing frequency in ac measurements. This and a lack of any magnetic diffraction peaks down to 2 K evidence a spin glass ground state.

$\text{CaFeFeNbO}_6$  is the first reported  $\text{AA'BB'O}_6$   $P4_2/n$  double double perovskite based on  $\text{A}' = \text{Fe}$ . As many  $\text{A/A'}$  columnar-ordered perovskites are based on  $\text{A}' = \text{Mn}$  but few with other metals, it is useful to compare synthesis pressures for analogue pairs;  $\text{CaATi}_2\text{O}_6$ ,  $\text{A}' = \text{Mn}$  (7 GPa)<sup>12</sup> and  $\text{Fe}$  (14–15 GPa);<sup>7</sup>  $\text{CaA'FeReO}_6$ ,  $\text{A}' = \text{Mn}$  (10 GPa)<sup>18</sup> and  $\text{Cu}$  (15.5 GPa);<sup>24</sup> and here  $\text{CaMFeNbO}_6$ ,  $\text{A}' = \text{Mn}$  (10 GPa) and  $\text{Fe}$  (14 GPa). The extra synthesis pressures for other  $\text{A}'$  cations relative to  $\text{Mn}^{2+}$  are in the range 4–8 GPa implying that further analogues of known  $\text{AMnBB'O}_6$  double double perovskites (synthesised at 10 GPa) may be accessible at pressure of 14 to 18 GPa for  $\text{A}' = \text{Fe}$ ,  $\text{Cu}$  and other divalent cations of a similar size. It is also notable that  $\text{CaFeTi}_2\text{O}_6$  was initially synthesised at 14–15 GPa, but crystals were subsequently grown at 12 GPa using water as a mineraliser, so pressures for growth of new double double perovskites may be lowered by a few GPa in the same way.

In conclusion,  $\text{CaFeFeNbO}_6$  is the first reported example of a  $P4_2/n$   $\text{AA'BB'O}_6$  double double perovskite based on  $\text{A}' = \text{Fe}$ . The synthesised samples are stoichiometric with  $\text{Fe}^{2+}/\text{Fe}^{3+}$  mixed valence, however, potentially interesting magnetic properties related to charge transfer are masked by antisite Fe/Nb disorder that leads to a spin glass ground state below a freezing transition at 12 K. The  $\text{CaMnFeNbO}_6$  analogue also shows substantial cation disorder and spin glassy behaviour. Comparison of optimum synthesis pressures for the latter and other pairs of ordered materials based on different A-site transition metals, suggests that pressures of at least 14–18 GPa will be required to discover the expected plethora of double double perovskites based on cations smaller than  $\text{Mn}^{2+}$ .

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## Conflicts of interest

There are no conflicts to declare.

## References

- G. King and P. M. Woodward, *J. Mater. Chem.*, 2010, **20**, 5785–5796; M. Shaikh, A. Fathima, M. J. Swamynadhan, H. Das and S. Ghosh, *Chem. Mater.*, 2021, **33**, 1594–1606; A. Ghosh, G. Palanichamy, D. P. Trujillo, M. Shaikh and S. Ghosh, *Chem. Mater.*, 2022, **34**, 7563–7578.
- M. T. Anderson, K. B. Greenwood, G. A. Taylor and K. R. Poeppelmeier, *Prog. Solid State Chem.*, 1993, **22**, 197–233.
- C. J. Howard, B. J. Kennedy and P. M. Woodward, *Acta Crystallogr., Sect. B: Struct. Sci.*, 2003, **59**, 463–471.
- S. Vasala and M. Karppinen, *Prog. Solid State Chem.*, 2015, **43**, 1–36.
- K.-I. Kobayashi, T. Kimura, H. Sawada, K. Terakura and Y. Tokura, *Nature*, 1998, **395**, 677–680.
- D. Serrate, J. De Teresa and M. Ibarra, *J. Phys.: Condens. Matter*, 2006, **19**, 023201.
- K. Lienenweber and J. Parise, *J. Solid State Chem.*, 1995, **114**, 277–281.
- G. Shimura, K. Niwa, Y. Shirako and M. Hasegawa, *Eur. J. Inorg. Chem.*, 2017, 835–839.
- A. A. Belik, L. Zhang, R. Liu, D. D. Khalyavin, Y. Katsuya, M. Tanaka and K. Yamaura, *Inorg. Chem.*, 2019, **58**, 3492–3501.
- R. Liu, D. D. Khalyavin, N. Tsunoda, Y. Kumagai, F. Oba, Y. Katsuya, M. Tanaka, K. Yamaura and A. A. Belik, *Inorg. Chem.*, 2019, **58**, 14830–14841.
- R. Liu, R. Scatena, D. D. Khalyavin, R. D. Johnson, Y. Inaguma, M. Tanaka, Y. Matsushita, K. Yamaura and A. A. Belik, *Inorg. Chem.*, 2020, **59**, 9065–9076.
- A. Aimi, D. Mori, K.-I. Hiraki, T. Takahashi, Y. J. Shan, Y. Shirako, J. Zhou and Y. Inaguma, *Chem. Mater.*, 2014, **26**, 2601–2608.
- M. Fukuda, T. Nishikubo, Z. Pan, Y. Sakai, M.-H. Zhang, S. Kawaguchi, H. Yu, Y. Okimoto, S.-Y. Koshihara, M. Itoh, J. Rödel and M. Azuma, *Inorg. Chem.*, 2020, **59**, 11749–11756.
- L. Zhang, Y. Matsushita, K. Yamaura and A. A. Belik, *Inorg. Chem.*, 2017, **56**, 5210–5218.
- E. Solana-Madruga, Á. M. Arévalo-López, A. J. Dos Santos-García, E. Urones-Garrote, D. Ávila-Brandé, R. Sáez-Puche and J. P. Attfield, *Angew. Chem., Int. Ed.*, 2016, **55**, 9340–9344.
- E. Solana-Madruga, Á. M. Arévalo-López, A. J. Dos Santos-García, C. Ritter, C. Cascales, R. Sáez-Puche and J. P. Attfield, *Phys. Rev. B*, 2018, **97**, 134408.
- K. Ji, Y. Yuan, G. T. Moyo, C. Ritter and J. P. Attfield, *J. Solid State Chem.*, 2022, **313**, 123329.
- G. M. McNally, Á. M. Arévalo-López, P. Kearins, F. Orlandi, P. Manuel and J. P. Attfield, *Chem. Mater.*, 2017, **29**, 8870–8874.
- G. M. McNally, A. M. Arévalo-López, F. Guillou, P. Manuel and J. P. Attfield, *Phys. Rev. Mater.*, 2020, **4**, 064408.
- E. Solana-Madruga, Y. Sun, Á. M. Arévalo-López and J. P. Attfield, *Chem. Commun.*, 2019, 55, 2605–2608.
- P. Kearins, E. Solana-Madruga, K. Ji, C. Ritter and J. P. Attfield, *J. Phys. Chem. C*, 2021, **125**, 9550–9555.
- E. Solana-Madruga, P. S. Kearins, K. N. Alharbi, C. T. Lennon, C. Ritter and J. P. Attfield, *Phys. Rev. Mater.*, 2021, **5**, 054412.
- K. Ji, K. N. Alharbi, E. Solana-Madruga, G. T. Moyo, C. Ritter and J. P. Attfield, *Angew. Chem., Int. Ed.*, 2021, **133**, 22422.
- E. Solana-Madruga, P. S. Kearins, C. Ritter, A. M. Arévalo-López and J. P. Attfield, *Angew. Chem., Int. Ed.*, 2022, **61**, e202209497.
- M. A. Patino, F. D. Romero, M. Goto, T. Saito, F. Orlandi, P. Manuel, A. Szabó, P. Kayser, K. H. Hong, K. N. Alharbi, J. P. Attfield and Y. Shimakawa, *Phys. Rev. Res.*, 2021, **3**, 043208.
- L. C. Chapon, P. Manuel, P. G. Radaelli, C. Benson, L. Perrott, S. Ansell, N. J. Rhodes, D. Raspino, D. Duxbury, E. Spill and J. Norris, *Neutron News*, 2011, **22**, 22–25.
- A. R. Chakhmouradian and R. H. Mitchell, *J. Solid State Chem.*, 1998, **138**, 272–277.
- N. Kashima, K. Inoue, T. Wada and Y. Yamaguchi, *Appl. Phys. A: Mater. Sci. Process.*, 2002, **74**(Suppl.), S805–S807.
- F. Kanamaru, H. Miyamoto, Y. Mimura, M. Koizumi, M. Shimada, S. Kume and S. Shin, *Mater. Res. Bull.*, 1978, **13**, 61–66.
- M. Ceretti, A. Piovano, A. Cousson, T. Berthier, M. Meven, G. Agostini, J. Schefer, O. Hernandez, C. Lamberti and W. Paulus, *CrystEngComm*, 2012, **14**, 5771–5776.

