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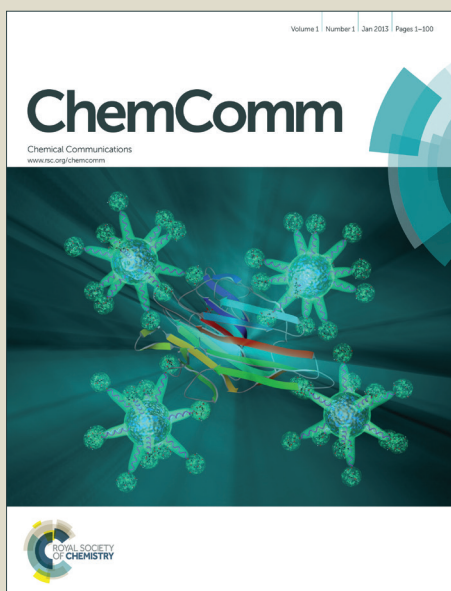
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## Stabilization of cubic Sr<sub>2</sub>FeMoO<sub>6</sub> through topochemical reduction †

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**Sr<sub>2</sub>FeMoO<sub>6</sub> has been extensively studied for application in spintronic devices. Through the topochemical de-intercalation of oxygen anions with metal hydride reduction, we demonstrate that the high temperature cubic phase is stabilized, at room temperature, whilst leaving the magnetic ordering intact. Synchrotron X-ray and neutron powder diffraction were used to characterize the structure and stoichiometry of the reduced oxide.**

Sr<sub>2</sub>FeMoO<sub>6</sub> (SFMO) is a half-metal (100% spin polarization of conduction electrons) with magnetic ordering above room temperature, making it a candidate for spintronic devices.<sup>1</sup> This half-metallic property is closely related to the antiferromagnetic ordering of nearest neighbor B-site cations in the double perovskite structure.<sup>2,3</sup> Electron doping has been identified as a promising method to increase the magnetic ordering temperature in double perovskites such as SFMO.<sup>4</sup> However, traditional cation solid-solution techniques tend to induce lattice strain. This strain has been linked to B-site disorder, or anti-site disorder (ASD), and is therefore detrimental to long range magnetic ordering.<sup>5,6</sup>

In this communication, we investigate the use of anion manipulation to electron dope SFMO and show that through oxygen de-intercalation, the high temperature cubic structure can be stabilized at room temperature without loss of the magnetic ordering. Recent developments in topochemical reductions have

highlighted their ability to selectively de-intercalate or substitute certain anions whilst leaving the rest of the lattice intact.<sup>7,8</sup> For example, SrFeO<sub>3-δ</sub> has been reduced to form the metastable antiferromagnet SrFeO<sub>2</sub>,<sup>9</sup> SrCrO<sub>3</sub> has been reduced to form the nanostructured material SrCrO<sub>3-δ</sub>,<sup>10</sup> and LaSrCoO<sub>4</sub> has been reduced to form the oxyhydride LaSrCoO<sub>3</sub>H<sub>0.7</sub>.<sup>11</sup> These reductions are performed by reacting a transition metal oxide with a strong solid-state reducing agent (e.g. CaH<sub>2</sub>, NaH, LiH) at low temperatures.<sup>12</sup> The topochemical reduction of ordered double perovskite systems is a relatively under explored area with the only published reports focused on the Sr<sub>n+1</sub>(Fe<sub>0.5</sub>Ru<sub>0.5</sub>)<sub>n</sub>O<sub>3n+1</sub> system.<sup>13,14</sup>

For this study, SFMO was first synthesized through the solid-state reaction of SrCO<sub>3</sub>, MoO<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub>. Stoichiometric amounts of the starting materials were thoroughly ground as an acetone slurry. After a 3 hour calcination at 900°C, pellets of the reaction mixture were heated in a tube furnace for 2.5 hours at 1200°C under flowing 5% H<sub>2</sub>/N<sub>2</sub> followed by furnace cooling. This final step was repeated three times, with intermittent grinding, to increase the crystallinity of the sample.

To prepare the reduced SFMO (SFMO-red), the oxide was ground thoroughly in a 1:3 mole ratio with CaH<sub>2</sub> in a N<sub>2</sub> filled glove box. Pellets of the reaction mixture were then sealed in glass ampoules (pressure <10<sup>-2</sup> Torr) and heated in a box furnace at 500°C for 3 days followed by furnace cooling. The reacted mixture was then washed with 0.15 M (mol/L) NH<sub>4</sub>Cl/dried methanol to remove reaction byproducts. The tetragonal to cubic phase transition was observed in samples reduced at temperatures as low as 400°C. However, in order to maximize the effects of the reaction, the highest reaction temperature that did not lead to sample decomposition (500°C) was used for all subsequent characterization experiments.

We investigated the structures of both SFMO and SFMO-red with high resolution synchrotron powder X-ray diffraction (S-XRD) and neutron powder diffraction (NPD) experiments. S-XRD patterns were collected on beam line 11-BM at the Advanced Pho-

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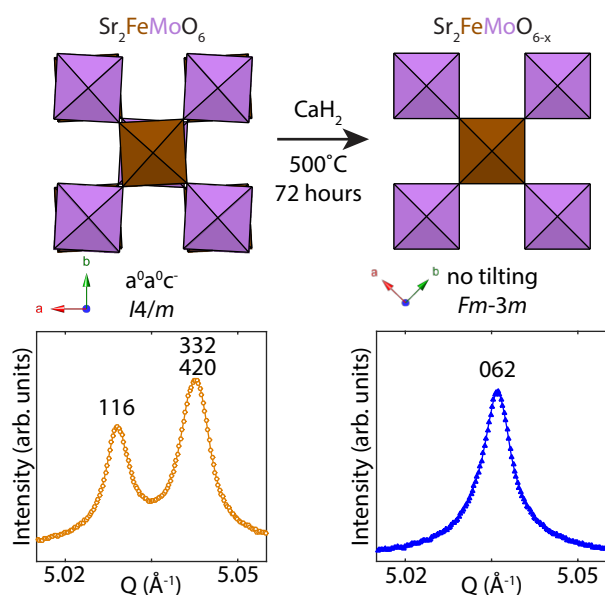
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**Fig. 1** Comparison of synchrotron XRD data of precursor (SFMO) and reduced (SFMO-red) materials. The reduction reaction eliminates the  $a^0a^0c^-$  octahedral tilting present in the starting material. A select region of the corresponding synchrotron XRD patterns are shown as the material transitions from tetragonal ( $I4/m$ ; left) to cubic ( $Fm\bar{3}m$ ; right). The Miller indices of the depicted peaks are included for reference. Complete diffraction patterns are provided in the ESI.<sup>†</sup>

ton Source (APS), Argonne National Laboratory, using an average wavelength of 0.413670 Å. Constant wavelength NPD data were collected on the BT-1 diffractometer at the NCNR using a Cu(311) monochromator with a 90° take-off angle,  $\lambda = 1.5398$  Å, and in-pile collimation of 60 minutes of arc. The sample was sealed in a vanadium container of length 50 mm and diameter 10.8 mm inside a dry He-filled glovebox. A furnace was used for temperature control. Rietveld refinement of S-XRD and NPD data was performed with the TOPAS 4.2<sup>15</sup> and FULLPROF<sup>16</sup> software suites.

A comparison of S-XRD data collected for SFMO and SFMO-red is presented in the bottom portion of Fig 1. A clear phase transition can be seen as the peak splitting observed for SFMO is no longer present in SFMO-red. This phase transition is associated with the loss of  $a^0a^0c^-$  (Glazer notation<sup>17</sup>) octahedral tilting, as is depicted in Fig. 1. Rietveld refinements were performed to quantify the affects of the reduction reaction with select parameters presented in Table 1. Complete structural parameters (Table S1) and plots of the refinements (Fig. S1 and S2) are given in the ESI.<sup>†</sup> The room temperature data (300 K) clearly indicate that whilst the  $I4/m$  structure fits the SFMO pattern, the  $Fm\bar{3}m$  structure best describes the symmetry of SFMO-red. This finding implies that the high temperature cubic structure of SFMO ( $T_s \approx 420$  K)<sup>18,19</sup> has been stabilized at room temperature through the topochemical hydride reduction. The slight increase in ASD observed in the refinement of SFMO-red may be an indication of increased lattice disorder that stabilizes the high temperature structure down to lower temperatures.

Such a stabilization of SFMO through electron doping has been

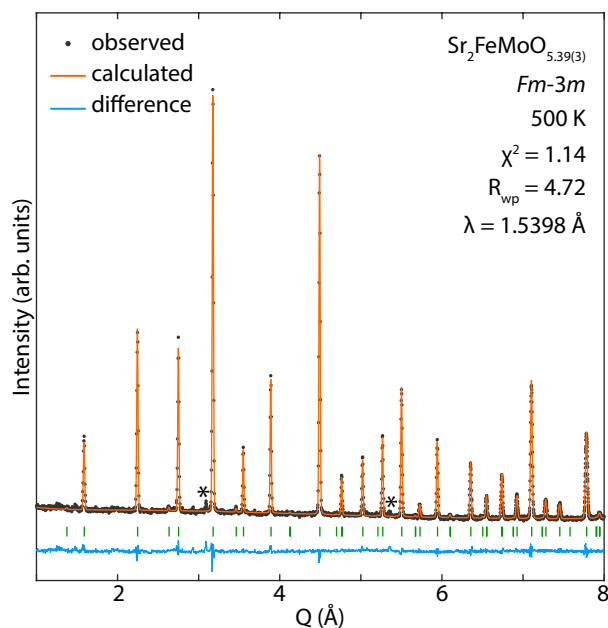
**Table 1** Select refinement parameters for diffraction patterns collected on  $Sr_2FeMoO_6$  and  $Sr_2FeMoO_{6-x}$  samples. ASD is the percent disorder in the B-site sublattice and rot. angle is the octahedral tilt angle. Complete refinement parameters are given in the ESI (Table S1).<sup>†</sup>

	$Sr_2FeMoO_6$		$Sr_2FeMoO_{6-x}$	
	300 K	500 K	300 K	500 K
Temperature	300 K	500 K	300 K	500 K
Technique	S-XRD	NPD	S-XRD	NPD
Space Group	$I4/m$	$Fm\bar{3}m$	$Fm\bar{3}m$	$Fm\bar{3}m$
$a$ (Å)	5.572022(7)	7.90784(6)	7.890986(7)	7.90795(6)
$c$ (Å)	7.90426(1)	-	-	-
vol. (Å <sup>3</sup> )	245.4069(7)	247.254(6) <sup>a</sup>	245.6766(6) <sup>a</sup>	247.264(6) <sup>a</sup>
ASD %	10.5(2)	-	14.0(2)	-
rot. angle (°)	7.93	0	0	0
bond lengths				
Fe-O1 (Å)	2.009(3)	2.003(3)	2.006(1)	2.001(4)
Fe-O2 (Å)	2.011(2)	-	-	-
bond lengths				
Mo-O1 (Å)	1.941(3)	1.951(3)	1.939(1)	1.953(4)
Mo-O2 (Å)	1.941(2)	-	-	-
O occ.	6.03(2)	6.00(3)	5.58(2)	5.39(3)
$\chi^2$	1.69	1.13	1.50	1.14
$R_{wp}$	10.09	7.33	8.38	4.72

<sup>a</sup> reduced unit cell volume for comparison to  $I4/m$  structure

previously reported in cases of A-site substitution of rare earth metals for Sr.<sup>20,21</sup> However, these reports also found that lattice strain, associated with cation doping, increases the ASD on the B-site sublattice. This increase in ASD leads to a rapid degradation of the magnetic ordering and therefore also the magnetoresistive properties. Topochemical reactions offer a promising alternative to more traditional doping techniques because the low temperatures of the reactions should disfavor significant rearrangement of the cation sublattice.<sup>7,8</sup>

Due to the limited sensitivity of X-rays to oxygen and hydrogen, NPD patterns were collected for SFMO and SFMO-red at 500 K. Above the magnetic ordering temperature ( $T_c \approx 420$  K), the nuclear Bragg reflections have no contribution from the magnetic structure factor, which allows us to accurately refine the oxygen structural parameters. Fig. 2 shows the refinement of SFMO-red, and select parameters are provided in Table 1. Complete refinement parameters (Table S1) and a plot of the SFMO refinement (Fig. S3) are given in the ESI.<sup>†</sup> The patterns for both samples were fit using the  $Fm\bar{3}m$  structure and the ASD was set to the value refined from S-XRD at 300 K. Previous reports have highlighted the insensitivity of NPD to ASD with refinement results of this parameter being unreliable.<sup>22</sup> However, even when the ASD parameters were allowed to vary freely, the refinements revealed no significant change in oxygen parameters. Fig. S4 (given in the ESI<sup>†</sup>) depicts a comparison of the NPD patterns for both samples, where it is clear that the reduced sample has a larger background than that of the precursor oxide. A possible reason for the observed heightened background in SFMO-red is the presence of

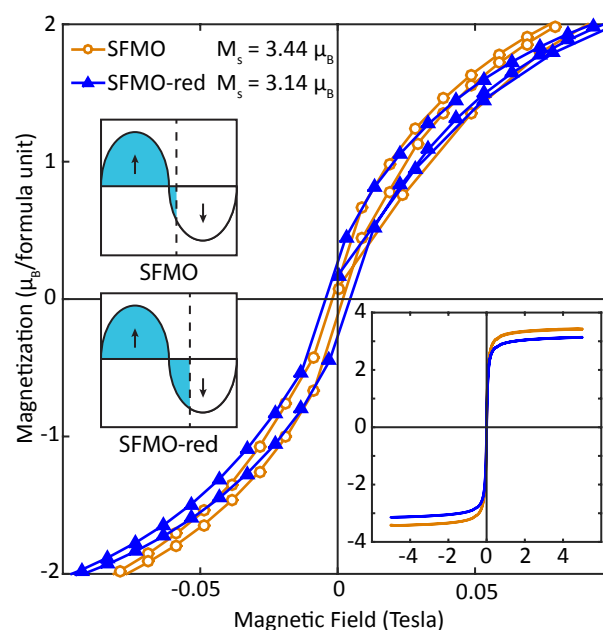


**Fig. 2** Neutron powder diffraction data of the reduced material (SFMO-red) collected at 500 K. The locations of the allowed reflections are given as green tick marks below the observed and calculated patterns. The asterisks indicate the locations of peaks due to the Nb furnace.

hydrogen, which has a large incoherent neutron scattering cross section.

The fits to the NPD data showed a change in the oxygen content from  $\text{Sr}_2\text{FeMoO}_{6.00(3)}$  to  $\text{Sr}_2\text{FeMoO}_{5.39(3)}$  for SFMO and SFMO-red, respectively. Previous efforts to reduce SFMO through more traditional methods have reported that the structure is not stable below an oxygen occupancy of  $\text{Sr}_2\text{FeMoO}_{5.915}$ <sup>23</sup> suggesting SFMO-red is a metastable phase. The determination of  $\text{Sr}_2\text{FeMoO}_{5.915}$  and other oxygen stoichiometries by Kircheisen and Töpfer,<sup>23</sup> however, were performed at high temperatures and is therefore unlike that of  $\text{Sr}_2\text{FeMoO}_{5.39(3)}$ , which was prepared at low temperatures and is stable at room temperature. Interestingly, the refined parameters of the fit for SFMO-red are largely unchanged at 500 K, except for the case of the oxygen occupancy. The unit cell volume increased by only 0.004% and the B-O bond lengths are all within error of one another for both the precursor and reduced material.

Given that hydride reductions of perovskites and perovskite related phases have led to oxyhydrides such as  $\text{LaSrCoO}_3\text{H}_{0.7}$ <sup>11</sup> and  $\text{BaTiO}_{3-x}\text{H}_x$ ,<sup>24,25</sup> we also considered the case where no vacancies are formed but rather  $\text{H}^-$  substitutes for  $\text{O}^{2-}$ . From this fit to the NPD data, a chemical stoichiometry of  $\text{Sr}_2\text{FeMoO}_{5.63(2)}\text{H}_{0.37(2)}$  was obtained for SFMO-red. From diffraction data alone, however, we are unable to differentiate between the two scenarios - oxygen de-intercalation or hydride substitution. The Rietveld technique is only able to refine the total scattering factor of a crystallographic site, which is given by the sum of all atoms occupying the site. Both scenarios would also lead to electron doping and therefore reduction of the metal oxidation states. Although we performed thermogravimetric analysis (TGA) measurements of SFMO-red under a stream of pure  $\text{O}_2$  for chemi-



**Fig. 3** Magnetic hysteresis loops of the starting material  $\text{Sr}_2\text{FeMoO}_6$  (SFMO) and the reduced product  $\text{Sr}_2\text{FeMoO}_{5.39(3)}$  (SFMO-red). The reduced material displayed a decrease in the saturated magnetic moment ( $M_s = 3.14 \mu_B$ ), compared to the starting material ( $M_s = 3.44 \mu_B$ ), as expected with electron doping. The reduced material also showed a slight increase in the coercive field. The inset density of states schematics illustrate how the filling of the conduction band (spin down) would affect the  $M_s$  value. The Fermi level is indicated by the dashed vertical line.

cal analysis, the TGA results did not further elucidate whether SFMO-red is an oxyhydride, a reduced oxide, or an oxide with hydroxyl groups since SFMO-red disproportionated to Mo-deficient SFMO and  $\text{SrMoO}_4$ . This result is unsurprising given that SFMO is formed under reducing conditions (5%  $\text{H}_2/\text{N}_2$ ) and SFMO-red itself is metastable.

To further explore the possible presence of H in this material, we performed prompt gamma activation analysis (PGAA) on both SFMO and SFMO-red at the NG-7 beam line at the NCNR. This spectroscopic technique allows for the accurate compositional analysis of elements in bulk samples. The analysis provided two interesting results. First, there is a measurable amount of H in the starting material, SFMO ( $\text{H}:\text{Mo} = 0.093(4)$ ). Second, the H content increases significantly with the reduction reaction with  $\text{H}:\text{Mo} = 0.246(8)$  for SFMO-red. The surprising presence of hydrogen in the precursor material likely arises from the preparation of SFMO under the 5%  $\text{H}_2/\text{N}_2$  stream and points to possible H content missed in previous studies of SFMO. Inelastic neutron scattering investigations are underway to elucidate the nature of H as being either protic ( $\text{H}^+$ ) or hydritic ( $\text{H}^-$ ) in these materials as PGAA does not probe this property. To remove surface water prior to analysis, both samples were dried overnight at 150 °C under vacuum.

Magnetic properties were measured using a magnetic property measurement system (Quantum Design MPMS XL) in DC mode. Fig. 3 presents a comparison of the hysteresis loops obtained for both SFMO and SFMO-red at 2 K. The saturated magnetic mo-

ment ( $M_s$ ), obtained under an applied magnetic field of 5 Tesla, was  $3.44 \mu_B$  and  $3.14 \mu_B$  for SFMO and SFMO-red, respectively. The  $M_s$  of SFMO agrees well with values found in the literature for samples containing approximately 10% ASD.<sup>26</sup> The decrease in  $M_s$  is expected with the reduction as the conduction band, which is aligned anti-parallel to the ferromagnetic moment, is populated by electrons.

A schematic representation of the spin-polarized density of states (DOS) is presented as an inset to Fig. 3. As the Fermi level increases (given as the dashed vertical line) into the spin down polarized conduction band, it can be seen that the net magnetic moment will decrease as the up and down spin polarized electrons cancel out. Population of the spin-down band, which is primarily of Fe and Mo  $t_{2g}$ -character,<sup>2</sup> could explain the stabilization of the cubic structure in SFMO-red. Such electronic stabilization is well known in metallic perovskite oxides such as  $\text{ReO}_3$  and  $\text{Na}_x\text{WO}_3$ , where filling of a metal  $t_{2g}$  band causes linear O-M-O bond angles and low electrical resistivity.<sup>27</sup>

To assess the effect of the reduction reaction on  $T_c$ , the magnetization was determined as a function of temperature (Fig. S5 in the ESI).<sup>†</sup> Whilst it is difficult to determine the exact temperature of the phase transition, it is apparent that  $T_c$  has not been largely affected and the magnetic ordering remains above 400 K. This finding implies that structural and magnetic phase transitions no longer coincide. Previous reports have established that these phase transitions are not coupled and doping can be used to affect them differently.<sup>5</sup> In these cases, however, the magnetic ordering was only ever observed in the tetragonal phase with the exception being cubic  $\text{Sr}_{2-x}\text{Eu}_x\text{FeMoO}_6$ .<sup>28</sup> Here, we have demonstrated that through the topochemical de-intercalation of oxygen atoms, we can stabilize the cubic phase at room temperature whilst leaving the magnetic ordering intact.

Fig. S6, provided in the ESI,<sup>†</sup> depicts a plot of  $M$  vs  $H$  data taken for SFMO and SFMO-red at 500 K. Here we can see that both SFMO and SFMO-red behave paramagnetically, as expected for a material above its  $T_c$ . However, the curve for SFMO-red, does not cross through the origin. This suggests there may be a small ferromagnetic impurity not detectable in any of our diffraction experiments.

In conclusion, we synthesized a reduced form of  $\text{Sr}_2\text{FeMoO}_6$  through a topochemical reduction reaction with  $\text{CaH}_2$ . Unlike its precursor, the new reduced oxide is cubic at room temperature whilst its magnetic ordering, known to be responsible for its magnetoresistive properties, remains intact. This is the first time that cubic SFMO has been stabilized at room temperature with such a large oxygen substoichiometry, demonstrating the promise of hydride reduction as a tool for the preparation of metastable functional materials. Our study highlights the possibility of using anion manipulation as a means to modulate the structure of functional materials as an alternative to traditional techniques of cation doping. A high incoherent background observed in the neutron diffraction data of SFMO-red and PGAA measurements indicate that the H content of the material may be responsible for the stabilization of SFMO-red. Ongoing studies on the hydride reduction of  $\text{Sr}_2\text{Fe}_{1+x}\text{Mo}_{1-x}\text{O}_6$  solid solutions will further establish the role of

the B cation in perovskites for either the de-intercalation of oxide anions or substitution of oxide by hydride.

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## References

- 1 K. L. Kobayashi, T. Kimura, H. Sawada, K. Terakura and Y. Tokura, *Nature*, 1998, **395**, 677–680.
- 2 D. Sarma, P. Mahadevan, T. Saha-Dasgupta, S. Ray and A. Kumar, *Physical Review Letters*, 2000, **85**, 2549–2552.
- 3 C. J. Howard, B. J. Kennedy and P. M. Woodward, *Acta Crystallographica Section B Structural Science*, 2003, **59**, 463–471.
- 4 M. Tovar, M. T. Causa, A. Butera, J. Navarro, B. Martinez, J. Fontcuberta and M. C. G. Passeggi, *Physical Review B - Condensed Matter and Materials Physics*, 2002, **66**, 1–5.
- 5 D. Serrate, J. M. D. Teresa and M. R. Ibarra, *Journal of Physics: Condensed Matter*, 2007, **19**, 023201.
- 6 O. Erten, O. N. Meetei, A. Mukherjee, M. Randeria, N. Trivedi and P. M. Woodward, *Physical Review Letters*, 2011, **107**, 257201.
- 7 T. Yamamoto and H. Kageyama, *Chemistry Letters*, 2013, **42**, 946–953.
- 8 M. A. Hayward, *Semiconductor Science and Technology*, 2014, **29**, 064010.
- 9 Y. Tsujimoto, C. Tassel, N. Hayashi, T. Watanabe, H. Kageyama, K. Yoshimura, M. Takano, M. Ceretti, C. Ritter and W. Paulus, *Nature*, 2007, **450**, 1062–5.
- 10 A. M. Arévalo-López, J. a. Rodgers, M. S. Senn, F. Sher, J. Farnham, W. Gibbs and J. P. Attfield, *Angewandte Chemie (International ed. in English)*, 2012, **51**, 10791–4.
- 11 M. A. Hayward, E. J. Cussen, J. B. Claridge, M. Bieringer, M. J. Rosseinsky, C. Kiely, S. J. Blundell, I. M. Marshall and F. L. Pratt, *Science (New York, N.Y.)*, 2002, **295**, 1882–4.
- 12 M. A. Hayward, M. A. Green, M. J. Rosseinsky and J. Sloan, *Journal of the American Chemical Society*, 1999, **121**, 8843–8854.
- 13 F. Denis Romero, S. J. Burr, J. E. McGrady, D. Gianolio, G. Cibin and M. A. Hayward, *Journal of the American Chemical Society*, 2013, **135**, 1838–44.
- 14 F. Denis Romero, D. Gianolio, G. Cibin, P. A. Bingham, J.-C. D'Hollander, S. D. Forder and M. A. Hayward, *Inorganic Chemistry*, 2013, **3**, 10920–10928.
- 15 R. W. Cheary and A. Coelho, *Journal of Applied Crystallography*, 1992, **25**, 109–121.
- 16 J. Rodríguez-Carvajal, *Physica B: Condensed Matter*, 1993, **192**, 55–69.
- 17 A. M. Glazer, *Acta Crystallographica Section B: Structural Science*, 1972, **B28**, 3384–3392.
- 18 O. Chmaissem, R. Kruk, B. Dabrowski, D. Brown, X. Xiong, S. Kolesnik, J. Jorgensen and C. Kimball, *Physical Review B*, 2000, **62**, 14197–14206.
- 19 S. Nakamura and K. Oikawa, *Journal of the Physical Society of Japan*, 2003, **72**, 3123–3127.
- 20 D. Serrate, J. M. Teresa, J. Blasco, M. R. Ibarra, L. Morellon and C. Ritter, *The European Physical Journal B*, 2004, **39**, 35–40.
- 21 Q. Zhang, G. Rao, Y. Xiao, H. Dong, G. Liu, Y. Zhang and J. Liang, *Physica B: Condensed Matter*, 2006, **381**, 233–238.
- 22 Q. Zhang, G. Liu and G. Rao, *Solid State Communications*, 2006, **138**, 294–298.
- 23 R. Kircheisen and J. Töpfer, *Journal of Solid State Chemistry*, 2012, **185**, 76–81.
- 24 Y. Kobayashi, O. J. Hernandez, T. Sakaguchi, T. Yajima, T. Roisnel, Y. Tsujimoto, M. Morita, Y. Noda, Y. Mogami, A. Kitada, M. Ohkura, S. Hosokawa, Z. Li, K. Hayashi, Y. Kusano, J. E. Kim, N. Tsuji, A. Fujiwara, Y. Matsushita, K. Yoshimura, K. Takegoshi, M. Inoue, M. Takano and H. Kageyama, *Nature materials*, 2012, **11**, 507–11.
- 25 T. Yajima, A. Kitada, Y. Kobayashi, T. Sakaguchi, G. Bouilly, S. Kasahara, T. Terashima, M. Takano and H. Kageyama, *Journal of the American Chemical Society*, 2012, **134**, 8782–5.
- 26 L. Balcells, J. Navarro, M. Bibes, A. Roig, B. Martinez and J. Fontcuberta, *Applied Physics Letters*, 2001, **78**, 781.
- 27 F. Cora, M. Stachiotti, C. Catlow and C. Rodríguez, *Journal of Physical Chemistry*, 1997, **5647**, 3945–3952.
- 28 Q. Zhang, Y. Xiao, Z. Xu, G. Liu, J. Li and G. Rao, *Journal of Solid State Chemistry*, 2010, **183**, 2432–2437.