Ferrimagnetism as a consequence of cation ordering in the perovskite LaSr₂Cr₂SbO₉

Emily C. Hunter*, Peter D. Battle*, Robert Paria Sena, Joke Hadermann

A R T I C L E   I N F O

Keywords:
Ferrimagnetism
Perovskite
Electron microscopy

A B S T R A C T

A polycrystalline sample of LaSr₂Cr₂SbO₉ has been synthesised using a standard ceramic method and characterized by x-ray and neutron diffraction, magnetometry and electron microscopy. The perovskite-related compound crystallises in the triclinic space group P1 with unit cell parameters of a=5.5344(6) Å, b=5.5562(5) Å, c=7.8292(7) Å, α=89.986(12)°, β=90.350(5)° and γ=89.926(9)° at room temperature. The two crystallographically-distinct, six-coordinate cation sites are occupied by Cr³⁺ and Sb⁵⁺ in ratios of 0.868(2):0.132(2) and 0.462(2):0.538(2). Ac and dc magnetometry revealed that LaSr₂Cr₂SbO₉ is ferrimagnetic below 150 K with a magnetisation of ~1.25 µB per formula unit in 50 kOe at 5 K. Neutron diffraction showed that the cations on the two sites order in a G-type arrangement with a mean Cr³⁺ moment of 2.17(1) µB at 5 K, consistent with a magnetisation of 1.32 µB per formula unit.

1. Introduction

Perovskite compounds have the general formula ABO₃ where A is usually a relatively-large divalent or trivalent cation and B is a smaller transition-metal or p-block cation. Due to the chemical flexibility of the perovskite structure, the complexity of these compounds can be increased by the partial substitution of either or both of the cations A and B. This has led to the formation of ‘double’, ‘triple’ and even ‘quadruple’ perovskites – an example of the latter being CaCu₃Fe₄O₁₂ [1]. The large range of accessible compositions has given rise to a plethora of electronic and magnetic properties among perovskite compounds; materials are known that show long-range magnetic order, magnetoresistance [2], giant magnetocaloric effects [3], multiferroic behaviour [4], quantum spin liquid behaviour [5] and relaxor ferroelectricity [6]. One relatively new phenomenon is relaxor ferromagnetism, with La₃Ni₂SbO₉ being the prime example, although Cr-Doped Nd₀.₅Ca₀.₅MnO₃ has also been described as relaxor ferromagnet [7,8]. La₃Ni₂SbO₉ or La₃Ni(Ni₀.₃₃Sb₀.₆₆₇)O₉ is a double perovskite that crystallises in the space group P2₁/n and has two crystallographically-distinct, six-coordinate sites, B and B’, that alternate in a 3D checkerboard pattern. One site is fully occupied by Ni²⁺ and the other is occupied by 33% Ni²⁺ and 67% Sb⁵⁺. This creates an ordered-disordered structure as there is complete cation ordering across the B sites but the nickel and antimony cations are randomly distributed over the B’ site. We originally prepared La₃Ni₂SbO₉ in the hope that the imbalance of magnetic cations on the two sites would lead to ferrimagnetism, even if the superexchange interactions between pairs of Ni²⁺ cations were antiferromagnetic. Magnetometry measurements indicated that La₃Ni₂SbO₉ does show a spontaneous magnetisation below 105 K but in early neutron diffraction measurements no magnetic Bragg scattering associated with long-range magnetic order was observed. However, in a later study the intensity of the 011 reflection was seen to increase as a function of applied magnetic field [9]. HAADF-STEM and EDX measurements provided evidence of a varying Sb/Ni stoichiometry across the sample and the presence of Sb-rich regions. Thus it was postulated that there were magnetically isolated ferrimagnetic regions in La₃Ni₂SbO₉ whose moments only became co-aligned on the application of a magnetic field. In this way La₃Ni₂SbO₉ can be compared to relaxor ferroelectrics such as Pb₃MgNb₂O₉ where a net polarisation is only observed on the application of an electric field [10]. It is likely that the occurrence of relaxor ferromagnetic behaviour is dependent on many factors such as the extent of the cation ordering across the B sites, the degree of tilting and rotation of the BO₆ octahedra, which will affect the relative strengths of competing superexchange interactions, and the electronic structure of the magnetic cation. To investigate the relative importance of these factors we have previously synthesised La₃Sr₃Ni₂TeO₉ [11] and Sr₃Fe₂TeO₉ [12]. We found that both compounds are markedly different to La₃Ni₂SbO₉ with Sr₃Fe₂TeO₉ exhibiting a mixture of nano-twinned 1:1 and 2:1 cation-ordered regions...
while La$_x$Sr$_{1-x}$Ni$_2$TeO$_6$ predominantly behaves as spin glass but also contains regions of both C- and G-type magnetic order. In a continuation of this work we have now investigated the effect of replacing the σ-mediated superexchange interactions of La$_x$Ni$_2$SbO$_6$ with the solely π-mediated superexchange interactions present in the novel compound La$_{0.479(3)}$Sr$_{0.521(3)}$Cr$_2$SbO$_6$[18]. This resulted in a good fit with $\chi^2$=2.331 and $R_m$=6.5%. The perovskite phase was found to be contaminated with 1.20(2) wt% Sr$_2$SbO$_7$. There was no evidence of strontium and lanthanum ordering over the A sites. Higher-resolution x-ray diffraction data were collected on instrument I11 at Diamond light source. A small shoulder was visible on the 200 reflection, which was identified as La$_2$O$_3$. Due the difficulty of separating the contributions of the two phases to the peak, a multi-phase refinement was carried out with the lattice parameters of La$_2$O$_3$ being fixed at the values reported by Qasim et al. [19]. This showed the sample to be contaminated by 1.36(3) wt% La$_2$O$_3$ and 1.58(2) wt% Sr$_2$SbO$_7$. The lattice parameters of the principal phase refined to values of $a=5.52788(11)$ Å, $b=5.55186(10)$ Å, $c=7.84306(16)$ Å and $\beta=90.308(1)^\circ$ in $P2_1/m$. Partial cation ordering over the six-coordinate sites was identified with a Cr$^{3+}$/Sb$^{5+}$ ratio of 0.854(3): 0.146(3) on the 2a site and 0.479(3):0.521(3) on the 2b site.

The molar magnetic susceptibility of La$_x$Sr$_{1-x}$Cr$_2$SbO$_6$ is shown as a function of temperature in Fig. 1. There is a divergence of the ZFC and FC curves below 150 K, with the FC molar susceptibility increasing faster than the ZFC molar susceptibility on cooling. Both susceptibility curves reach a maximum before decreasing slightly on further cooling; the FC susceptibility reaches a maximum of 4.54 cm$^3$ mol$^{-1}$ at 14 K and the ZFC reaches 2.24 cm$^3$ mol$^{-1}$ at 40 K. $\chi^r(T)$ cannot be considered to be linear below 250 K. Only the data in the temperature range 250$\pm$5 K on the 2a site were therefore fitted to the Curie-Weiss law, resulting in values of 2.5(2) $\mu_B$ and +62(10) K for the effective magnetic moment per Cr$^{3+}$ cation and the Weiss constant, respectively. The high standard deviations are a consequence of the need to use only a limited temperature range in the data analysis. The field dependence of the magnetisation for formula unit is shown in Fig. 2. $M(H)$ is linear at 250 K, well above the magnetic transition temperature of 150 K, but non-linear at 5 K where a weak hysteresis is observed. The remanent magnetisation is $-0.10\mu_B$ per formula unit, the coercive field is 0.2 kOe and the saturation magnetisation is tending towards $-1.25\mu_B$ per formula unit. Below 150 K the ac susceptibility, see Fig. 3, is a function of frequency and complex. At each frequency, both the real and imaginary components show maxima at temperatures between 60 and 80 K; the frequency dependence is most obvious close to the temperature of the susceptibility maximum. The parameter $\Delta T/I_0\Delta\log(\omega)$ takes a value of 0.032, which is within the range expected for a canonical spin glass [20].

3. Results

The X-ray diffraction pattern collected on the Empyrean diffractometer was initially analysed in the space group $I2/m$, as reported for Sr$_2$Cr$_2$O$_7$[18]. This resulted in a good fit with $\chi^2$=2.331 and $R_m$=6.5%. The perovskite phase was found to be contaminated with 1.20(2) wt% Sr$_2$SbO$_7$. There was no evidence of strontium and lanthanum ordering over the A sites. Higher-resolution x-ray diffraction data were collected on instrument I11 at Diamond light source. A small shoulder was visible on the 200 reflection, which was identified as La$_2$O$_3$. Due the difficulty of separating the contributions of the two phases to the peak, a multi-phase refinement was carried out with the lattice parameters of La$_2$O$_3$ being fixed at the values reported by Qasim et al. [19]. This showed the sample to be contaminated by 1.36(3) wt% La$_2$O$_3$ and 1.58(2) wt% Sr$_2$SbO$_7$. The lattice parameters of the principal phase refined to values of $a=5.52788(11)$ Å, $b=5.55186(10)$ Å, $c=7.84306(16)$ Å and $\beta=90.308(1)^\circ$ in $P2_1/m$. Partial cation ordering over the six-coordinate sites was identified with a Cr$^{3+}$/Sb$^{5+}$ ratio of 0.854(3): 0.146(3) on the 2a site and 0.479(3):0.521(3) on the 2b site.
facilitates comparison with other monoclinic and orthorhombic perovskites. The refined lattice parameters at room temperature are $a=5.5344(6)\ \text{Å}$, $b=5.5562(5)\ \text{Å}$, $c=7.8292(7)\ \text{Å}$, $\alpha=89.986(12)^\circ$, $\beta=90.350(5)^\circ$, $\gamma=89.926(9)^\circ$ and at $5\ K$ are $a=5.5239(5)\ \text{Å}$, $b=5.5546(5)\ \text{Å}$, $c=7.8081(7)\ \text{Å}$, $\alpha=89.8703(18)^\circ$, $\beta=90.2482(18)^\circ$, $\gamma=90.103(5)^\circ$. Statistically significant distortions away from a monoclinic lattice are thus present at both temperatures. The x-ray diffraction data collected on 111 were re-analysed using the space group and oxygen coordinates derived from the neutron refinement and the final fit is shown in Fig. 4. The extent of the B site cation order remained effectively unchanged in this new model with the $\text{Cr}^{3+}$:$\text{Sb}^{5+}$ ratio on the 2g site being $0.868(2)$ wt% $\text{Sr}_2\text{Sb}_2\text{O}_7$ and $1.36(3)$ wt% $\text{LaCrO}_3$ detected. From the neutron data, $1.80(4)$ wt% $\text{Sr}_2\text{Sb}_2\text{O}_7$ and $1.80(6)$ wt% $\text{LaCrO}_3$ were detected at $300\ K$.

The 111 data gave a much smaller error on the occupancies of the B sites than the GEM data and so the occupancies were fixed to those derived from the 111 data during the final analysis of both the $300\ K$ and $5\ K$ neutron datasets. The neutron diffraction patterns collected at $5\ K$ and $300\ K$ from the $34.96^\circ$ and $91.30^\circ$ banks are shown in Figs. 5 and 6. The neutron patterns collected on the $63.62^\circ$ and $154.40^\circ$ banks are included in Figs. S1 and S2 in the Supporting information. These four banks were refined simultaneously to determine the structural parameters, which are listed in Tables 1, 2, and selected bond lengths and angles are given in Tables 3, 4. The crystal structure of $\text{LaSr}_2\text{Cr}_2\text{SbO}_9$ at room temperature is shown in Fig. 7. Comparison of the neutron diffraction patterns collected at $5\ K$ and $300\ K$ shows that there is additional intensity in the $011$ and $121$ reflections at $5\ K$. Since this additional intensity is only apparent at high $d$-spacings it was assumed to be magnetic in origin and it could accounted for by the addition of a G-type magnetically-ordered phase, see Fig. 8. Assuming that the whole sample orders antiferromagnetically, see below, the best fit was obtained when nearest-neighbour spins were set to be aligned antiparallel along [001] giving a refined $\text{Cr(III)}$ moment of $2.17(1)\ \mu\text{B}$. This gives an overall net magnetisation of $1.32\ \mu\text{B}$ per formula unit, which is in excellent agreement with the saturation magnetisation obtained from $M(H)$ at $5\ K$.

Selected-area electron diffraction (SAED) patterns were taken of the different zones, usually connected in tilt series, from many crystallites. Note that because the cell parameters and angles only deviate slightly from those of the cubic parent perovskite, it is impossible with transmission electron microscopy to differentiate geometrically between [100], [1-11], [111], [010], [1-1-1] and [11-1] ($c < 110 >_p$ refers to the parent perovskite cell), and also between [001], [1-10] and [110] ($c < 100 >_p$). However, since all $< 110 >_p$ and $< 100 >_p$ ob-
observed showed the same body-centered patterns, we can conclude that the reflection conditions are $hkl$: $h+k+l=2n$, $h0l$: $h+k=2n$, $hk0$: $h+l=2n$, $h0k$: $h=2n$, $0k0$: $k=2n$, consistent with the space group and unit cell derived from the neutron diffraction data. Representative patterns along the $<110>_{P}$ and $<100>_{P}$ zones are shown in Fig. 9. The underlined indices on these patterns represent one of the possible indexations using the supercell obtained from XRD.

The atomic-resolution HAADF-EDX map shown in Fig. 10 confirms that there is no ordering of Sr and La on the A site. On the B position there is an alternation in signal intensity for both Cr and Sb, but in a complementary way, as is also very clear from the combined map shown at the bottom right of the figure, i.e. both elements are present on both positions but Cr dominates one position and Sb the other. This is in agreement with the site occupancies determined from the x-ray diffraction data.

4. Discussion

LaSr$_2$Cr$_2$SbO$_9$ was synthesised in order to provide a perovskite analogue of La$_8$Ni$_6$SbO$_9$ that could be used in a comparison of the magnetic behaviour of a $d^8$ cation, where $\sigma$ superexchange interactions are dominant, with that of a $d^3$ cation where $\pi$ superexchange interactions are dominant. However, we have found that the structures are not directly comparable as La$_8$Ni$_6$SbO$_9$ crystallises in the monoclinic space group $P2_1/n$ whereas LaSr$_2$Cr$_2$SbO$_9$, or La$_{0.666}$Sr$_{1.333}$Cr$_{1.333}$Sb$_{0.667}$O$_6$ crystallises in the triclinic space group $\tilde{P}$. This group is uncommon amongst double perovskites but other examples include Ba$_2$LaRuO$_6$ [21] and Sr$_2$FeRuO$_6$ [22]. These space groups are similar in that they both introduce two crystallographically-distinct six-coordinate cation sites and three independent oxygen positions, thus allowing the BO$_6$ octahedra to tilt about each of the three unit cell axes. However, the key difference is that the rotations of successive octahedra are out of phase along all three axes in $\tilde{P}$ whereas in $P2_1/n$ two of the rotations are out of phase and one is in-phase [23]. These tilts and rotations are smaller in LaSr$_2$Cr$_2$SbO$_9$, as is reflected by the B–O–B bond angles given in Table 4. All three bond angles in LaSr$_2$Cr$_2$SbO$_9$ are larger than those in La$_8$Ni$_6$SbO$_9$, the average B–O–B′ bond angles being 167.1$^\circ$ and 154.1$^\circ$ respectively at 300 K. The fact that the B–O–B′ bond angles are much closer to 180$^\circ$ in LaSr$_2$Cr$_2$SbO$_9$ means that the antiferromagnetic superexchange interactions are likely to be much stronger than in La$_8$Ni$_6$SbO$_9$.

Another important difference between the two compounds is that there is full B-site ordering in La$_8$Ni$_6$SbO$_9$ whereas in LaSr$_2$Cr$_2$SbO$_9$ there is a partial mixing of the cations such that the 2g site is only 86.8% occupied by Cr$^{3+}$. This is not surprising given that there are smaller differences in charge and size between Cr$^{3+}$ and Sb$^{5+}$ than between Ni$^{2+}$ and Sb$^{5+}$. This increased site disorder makes it more probable that a Cr$^{3+}$ cation will be surrounded by one of more NN antimony cations.

In a perovskite compound there are three types of superexchange interaction between six-coordinate cations. These are nearest-neighbour (J1), next-nearest neighbour (J2) and third nearest-neighbour (J3) superexchange interactions as illustrated in Fig. 11. To eliminate the effect of the J1 interaction one can look at the cation-ordered perovskites Sr$_2$CrSbO$_6$ and Ca$_2$CrSbO$_6$, where in both cases there is nearly complete 1:1 ordering of the B-site cations [24]. The mean B–O–B′ bond angle of Sr$_2$CrSbO$_6$ is comparable to LaSr$_2$Cr$_2$SbO$_9$ at...
169.2°, while the mean B–O–B′ bond angle of Ca₄CrSbO₆ is closer to that of La₂SrNi₂TeO₉ at 152.47°. Sr₂CrSbO₆ is an A-Type antiferromagnet with Tₐ=12 K and Ca₃SrNi₂TeO₉ is a ferromagnet with Tₑ=16 K. LaSr₂Cr₂SbO₉ has a ferrimagnetic transition temperature of 150 K, which is too high a temperature to be attributable to the J₃ interaction as demonstrated by CaCu₃Ti₄O₁₂, where the antiferromagnetic order below 25 K has been shown by x-ray absorption spectroscopy to originate from the Cu-O-Ti-O-Cu superexchange path [25]. The transition is also much higher in temperature than the J₂-driven antiferromagnetic transition of Sr₂CrSbO₆, so it is possible that this feature is caused by the increase in signiﬁcance of J₂ and J₃ superexchange interactions.

Magnetic moment of Cr³⁺=2.17(1)µB as demonstrated by CaCu₃Ti₄O₁₂, where the antiferromagnetic order below 25 K has been shown by x-ray absorption spectroscopy to originate from the Cu-O-Ti-O-Cu superexchange path [25]. The transition is also much higher in temperature than the J₂-driven antiferromagnetic transition of Sr₂CrSbO₆, so it is possible that this feature is caused by the increase in signiﬁcance of J₂ and J₃ superexchange interactions.

Table 1
Structural parameters of LaSr₂Cr₂SbO₉ at room temperature.

| Atom         | Site | x     | y     | z     | Uₑₑ/Å² | Occupancy |
|--------------|------|-------|-------|-------|--------|-----------|
| Sr/La        | 4i   | 0.5014(17) | 0.4992(10) | 0.2469(11) | 0.00886(20) | Sr: 0.6667 |
|              |      |        |       |       |        | La: 0.3333  |
| Cr/Sb1       | 2f   | 0     | ½     | 0     | 0.00115(13) | Cr: 0.462(2) |
| Cr/Sb2       | 2g   | ½     | 0     | 0     | 0.00115(13) | Sr: 0.538(2) |
| Sr/La        | 01   | 0.2577(12) | 0.2587(14) | −0.0215(8) | 0.0053(7) | 1         |
| Sr/La        | 02   | 0.2307(15) | 0.7690(13) | 0.0164(18) | 0.0088(7) | 1         |
| Sr/La        | 03   | 0.4877(12) | 0.0500(5)  | 0.2497(9)  | 0.0074(6) | 1         |

Rₑₑ=3.25%, R_p=2.52%, χ=3.698
Space group II: a=5.5344(6) Å, b=5.5562(5) Å, c=7.8292(7) Å, α=89.986(12)°, β=90.350(5)°, γ=90.926(9)°.

Table 2
Structural parameters of LaSr₂Cr₂SbO₉ at 5 K.

| Atom         | Site | x     | y     | z     | Uₑₑ/Å² | Occupancy |
|--------------|------|-------|-------|-------|--------|-----------|
| Sr/La        | 4i   | 0.4981(19) | 0.4980(5)  | 0.2500(10) | 0.00650(14) | Sr: 0.6667 |
|              |      |        |       |       |        | La: 0.3333  |
| Cr/Sb1       | 2f   | 0     | ½     | 0     | 0.00039(11) | Cr: 0.462(2) |
| Cr/Sb2       | 2g   | ½     | 0     | 0     | 0.00039(11) | Sr: 0.538(2) |
| Sr/La        | 01   | 0.2614(11) | 0.2622(189) | −0.0263(7) | 0.00643(58) | 1         |
| Sr/La        | 02   | 0.2441(11) | 0.7563(81) | 0.0234(5)  | 0.00421(52) | 1         |
| Sr/La        | 03   | 0.5054(13) | 0.0511(26)  | 0.2501(8)  | 0.00485(30) | 1         |

Rₑₑ=3.14%, R_p=2.82%, χ=3.736
Space group II: a=5.5239(5) Å, b=5.5545(5) Å, c=7.8081(7) Å, α=89.8703(18)°, β=90.2482(18)°, γ=90.1035(5)°.
Magnetic moment of Cr³⁺=2.17(1)µB

Table 3
Selected bond lengths (Å) in LaSr₂Cr₂SbO₉ at room temperature and 5 K.

| Bond     | Room temperature | 5 K |
|----------|------------------|-----|
| Sr/La – O | 2.595(8)         | 2.568(4) |
| Sr/La – O | 2.712(12)        | 2.702(11) |
| Sr/La – O | 2.827(13)        | 2.839(11) |
| Sr/La – O | 2.602(8)         | 2.612(6)  |
| Sr/La – O | 2.768(15)        | 2.671(10) |
| Sr/La – O | 2.776(14)        | 2.859(10) |
| Sr/La – O | 2.497(5)         | 2.483(4)  |
| Sr/La – O | 2.721(12)        | 2.755(13) |
| Sr/La – O | 2.841(12)        | 2.786(13) |
| Sr/La – O | 2.704            | 2.698    |
| Sr/Sb1 – O | 1.964(7)        | 1.970(6)  |
| Sr/Sb1 – O | 1.971(9)        | 1.967(6)  |
| Sr/Sb1 – O | 1.980(7)        | 1.972(6)  |
| Sr/Sb2 – O | 1.971(7)        | 1.976(6)  |
| Sr/Sb2 – O | 1.973(9)        | 1.964(6)  |
| Sr/Sb2 – O | 1.977(7)        | 1.974(6)  |
| Sr/Sb2 – O | 1.974            | 1.971    |

Temperature akin to that of a spin glass. Furthermore, the refined Cr(III) moment at 5 K of 2.17(1) µB and the effective moment of 2.54(18) µB extracted from the Curie-Weiss fit are both lower than the expected values of ~2.5 µB and 3.7–3.9 µB [26]. Similar behaviour was seen in our study of La₃Ni₂SbO₉ [7,9]. In that case, a moment of 2.2(1) µB per Ni²⁺ cation was extracted from the Curie-Weiss fit, rather than the expected 2.83 µB, and no magnetic scattering was present in the neutron diffraction pattern [7]. In the present case we cannot place too much emphasis on the value of the effective moment because our data do not extend very far above the temperature of the ferrimagnetic transition. The moment refined from the neutron diffraction data is always expected to be reduced from the theoretical value of 3 µB by covalency in the Cr–O bonds, but the observed value is lower than in those reported in simple, comparable compounds, for example 2.63(3).
µB in LaCrO3 [27]. (However, we must point out that an even lower Cr(III) moment of 1.64(4) µB was reported for Sr2CrSbO6 [24].) One possible explanation for the frequency dependence of the transition temperature and the reduced value of the ordered moment is that the entire sample is not involved in long-range magnetic order due to the disruption caused by the presence of Sb-O-Sb NNs and variations in the relative strengths of competing superexchange interactions in the affected regions. We have previously argued that in La3Ni2SbO9 there are magnetically isolated domains that only co-align to give long-range magnetic order on the application of an applied magnetic field. While the majority of LaSr2Cr2SbO9 clearly exhibits long-range magnetic order that is detectable by neutron diffraction there may still be some magnetically isolated regions that do not contribute to the magnetic Bragg peaks. If we assume that there are regions of the sample that are not fully ordered and assign each ordered Cr(III) a moment of 2.6 µB then only 83.5(4)% of our sample is involved in the long-range G-type magnetic order. We propose that the remaining atomic moments behave in a glassy fashion and are thus responsible for the frequency dependence of the ac susceptibility.

5. Conclusion

Our attempts to make a ferrimagnet based on the unequal occupation by magnetic cations of two distinct but similar sites failed in the case of La3Ni2SbO9 but they have succeeded in the case of LaSr2Cr2SbO9, which orders ferrimagnetically below 150 K. However, not all of the Cr3+ ions are involved in the long-range magnetic order; the decoupled spins behave in a glass-like manner. It has been argued that, as a consequence of small differences in the crystal structures, stronger superexchange interactions are present in LaSr2Cr2SbO9 than in La3Ni2SbO9 and La2SrNi2TeO9 and that the increase in strength facilitates the establishment of magnetic coherence in the former, despite the presence of cation disorder, rather than the formation of a dominant spin-glass phase, as occurs in La2SrNi2TeO9 or the forma-

Table 4

| LaSr2Cr2SbO9 | Room temperature | 5 K |
|---------------|------------------|-----|
| O1 – Cr/Sb1 – O2 | 93.02(28)x2 | 90.41(24)x2 |
| O1 – Cr/Sb1 – O3 | 91.80(26)x2 | 91.29(17)x2 |
| O2 – Cr/Sb1 – O3 | 91.3(5)x2 | 91.40(20)x2 |
| O1 – Cr/Sb2 – O2 | 91.94(28)x2 | 92.13(24)x2 |
| O1 – Cr/Sb2 – O3 | 92.62(27)x2 | 90.14(18)x2 |
| O2 – Cr/Sb2 – O3 | 90.2(5)x2 | 90.97(19)x2 |
| Cr/Sb1 – O1 – Cr/Sb2 | 169.5(4) | 166.90(26) |
| Cr/Sb1 – O2 – Cr/Sb2 | 168.5(4) | 168.98(23) |
| Cr/Sb1 – O3 – Cr/Sb2 | 163.36(17) | 163.35(11) |
| Cr/Sb1 – O – Cr/Sb2 | 167.12 | 166.41 |
| La3Ni2SbO9 | Ni/Sb1 – O1 – Ni/Sb2 | 151.62(1) | 151.3(3) |
| Ni/Sb1 – O2 – Ni/Sb2 | 155.62(1) | 155.7(3) |
| Ni/Sb1 – O3 – Ni/Sb2 | 155.12(1) | 154.7(2) |
< Ni/Sb1 – O – Ni/Sb2 | 154.12 | 153.9 |
| La2SrNi2TeO9 | Ni/Te1 – O1 – Ni/Te2 | 159.7(4) | 160.8(5) |
| Ni/Te1 – O2 – Ni/Te2 | 159.3(4) | 157.4(5) |
| Ni/Te1 – O3 – Ni/Te2 | 158.8(2) | 158.1(2) |
< Ni/Te1 – O – Ni/Te2 | 159.3 | 158.8 |

Fig. 7. The crystal structure of LaSr2Cr2SbO9 generated from the structural parameters refined from the GEM data collected at 300 K. Green and yellow octahedra represent BO6 and B′O6 octahedra, respectively. The A cations are represented by blue circles. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 8. The G-type antiferromagnetic structure adopted by LaSr2Cr2SbO9.
tion of ferrimagnetic microdomains, as occurs in La$_3$Ni$_2$SbO$_9$. Thus it is appropriate to call LaSr$_2$Cr$_2$SbO$_9$ a frustrated ferrimagnet rather than a relaxor ferromagnet.

Acknowledgments

Experiments at the ISIS Pulsed Neutron and Muon Source were supported by the STFC. We are grateful to I. da Silva for the assistance provided at ISIS and to the EPSRC for financial support under Grant EP/M018954/1. We also thank Diamond Light Source Ltd (EE13284) for the award of beamtime.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2017.01.024.

References

[1] I. Yamada, M. Murakami, N. Hayashi, S. Mori, Inverse charge transfer in the quadruple perovskite CaCu$_6$F$_2$O$_{12}$, Inorg. Chem. 55 (2016) 1715–1719.
[2] J. Navarro, L.I. Balcells, F. Sandiumenge, M. Bibes, A. Roig, B. Martinez, J. Fontcuberta, Antisite defects and magnetoresistance in Sr$_2$FeMoO$_6$ double perovskite, J. Phys.: Condens. Matter 13 (2001) 8481.

[3] J.K. Murthy, K.D. Chandrasekhar, S. Mahana, D. Topwal, A. Veniaminov, Giant magnetocaloric effect in Gd$_2$NiMnO$_4$ and Gd$_2$CoMoO$_4$ ferromagnetic insulators, J. Phys. D: Appl. Phys. 48 (2015) 355001.

[4] M.P. Singh, K.D. Truong, P. Fournier, P. Rauwel, E. Rauwel, L.P. Carignan, D. Ménard, A radical approach to promote multiferroic coupling in double perovskites, J. Magn. Magn. Mater. 321 (2009) 1743–1747.

[5] T. Dey, A.V. Mahajan, R. Kumar, B. Koteswararao, F.C. Chou, A.A. Omrani, H.M. Ronnow, Possible spin-orbit driven spin-liquid ground state in the double perovskite phase of Ba$_3$YIr$_2$O$_9$, Phys. Rev. B 88 (2013) 134425.

[6] A.A. Bokov, Z.G. Ye, Recent progress in relaxor ferroelectrics with perovskite structure, J. Mater. Sci. 41 (2006) 31–52.

[7] P.D. Battle, S.I. Evers, E.C. Hunter, M. Westwood, La$_3$Ni$_2$SbO$_9$: a relaxor ferromagnet, Inorg. Chem. 52 (2013) 6648–6653.

[8] T. Kimura, Y. Tomioka, R. Kumai, Y. Okimoto, Y. Tokura, Diffuse phase transition and phase separation in Cr-doped Nd$_{1/3}$Ca$_{1/3}$MnO$_3$: a relaxor ferromagnet, Phys. Rev. Lett. 83 (1999) 3940–3943.

[9] P.D. Battle, M. Avdeev, J. Hadermann, The interplay of microstructure and magnetism in La$_3$Ni$_2$SbO$_9$, J. Solid State Chem. 220 (2014) 163–166.

[10] P.K. Davies, M.A. Akbas, Chemical order in PMN-related relaxors: structure, stability, modification, and impact on properties, J. Phys. Chem. Solids 61 (2000) 159–166.

[11] R. Paria Sena, J. Hadermann, C.-M. Chin, E.C. Hunter, P.D. Battle, Structural chemistry and magnetic properties of the perovskite SrLa$_2$Ni$_2$TeO$_6$, J. Solid State Chem. 243 (2016) 304–311.

[12] Y. Tang, E.C. Hunter, P.D. Battle, R.P. Sena, J. Hadermann, M. Avdeev, J.M. Cadogan, Structural chemistry and magnetic properties of the perovskite Sr$_2$Fe$_2$TeO$_6$, J. Solid State Chem. 242 (2016) 86–95.

[13] H.M. Rietveld, A profile refinement method for nuclear and magnetic structures, J. Appl. Crystallogr. 2 (1969) 65–71.

[14] Larson, A.C., Von Dreele, R. B., Los Alamos Natl. Lab. Rep. LAUR 1994, 86-748.

[15] Argonne National Laboratory Compute X-ray Absorption. (http://11bm.xray.aps.anl.gov/absorb/absorb.php).

[16] W.F. David, Powder diffraction peak shapes. Parameterization of the pseudo-Voigt as a Voigt function, J. Appl. Crystallogr. 19 (1986) 63–64.

[17] NIST Center for Neutron Research Neutron Attenuation and Activation. (https://www.ncnr.nist.gov/instruments/bt1/neutron.html).

[18] A. Faik, J.M. Igartua, M. Gateshki, G.J. Cuello, Crystal structures and phase transitions of Sr$_3$CrSbO$_6$, J. Solid State Chem. 182 (2009) 1717–1725.

[19] I. Qasim, P.E.R. Blanchard, S. Liu, B.J. Kennedy, M. Avdeev, Impact of Cu doping on the structure and electronic properties of LaCr$_{1-y}$Cu$_y$O$_3$, Inorg. Chem. 53 (2014) 2240–2247.

[20] J.A. Mydosh, Spin Glasses, Taylor & Francis Ltd, London, 1993.

[21] P.D. Battle, J.B. Goodenoough, R. Price, The crystal structures and magnetic properties of Ba$_2$LaRuO$_6$ and Ca$_2$LaRuO$_6$, J. Solid State Chem. 46 (1983) 234–244.

[22] P.D. Battle, G.R. Blake, T.C. Gibb, J.F. Vente, Structural chemistry and electronic properties of Sr$_2$FeIrO$_6$, J. Solid State Chem. 145 (1999) 541–548.

[23] P.M. Woodward, Octahedral tilting in perovskites. I. geometrical considerations, Acta Crystallogr. Sect. B 53 (1997) 32–43.

[24] M. Retuerto, M. García-Hernandez, M.J. Martinez-Lope, J.A. Alonso, Switching from ferro- to antiferromagnetism in A$_2$CrSbO$_6$ (A = Ca, Sr) double perovskites: a neutron diffraction study, J. Mater. Chem. 17 (2007) 3555–3561.

[25] M. Mizumaki, T. Saito, H. Shiraki, Y. Shimakawa, Orbital hybridization and magnetic coupling of the A-site Cu spins in CaCu$_3$B$_4$O$_{12}$ (B=Ti, Ge, and Sn) perovskites, Inorg. Chem. 48 (2009) 3499–3501.

[26] K. Burger, Coordination Chemistry: Experimental Methods, Butterworth, London, 1973.

[27] M. Tseggai, P. Nordblad, R. Tellgren, H. Rundlöf, G. Andrè, F. Bourèe, Synthesis, nuclear structure, and magnetic properties of LaCr$_{1-y}$Mn$_y$O$_3$ (y=0, 0.1, 0.2, and 0.3), J. Alloy. Compd. 457 (2008) 532–540.