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Structural chemistry and magnetic properties of the perovskite $SrLa_2Ni_2TeO_9$

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ABSTRACT

A polycrystalline sample of $SrLa_2Ni_2TeO_9$ has been synthesized using a standard ceramic method and characterized by neutron diffraction, magnetometry and electron microscopy.

The compound adopts a monoclinic, perovskite-like structure with space group $P2_1/n$ and unit cell parameters $a=5.6008(1)$, $b=5.5872(1)$, $c=7.9018(2)$ Å, $\beta=90.021(6)^\circ$ at room temperature. The two crystallographically-distinct B sites are occupied by Ni^{2+} and Te^{6+} in ratios of 83:17 and 50:50.

Both ac and dc magnetometry suggest that the compound is a spin glass below 35 K but the neutron diffraction data show that some regions of the sample are antiferromagnetic. Electron microscopy revealed twinning on a nanoscale and local variations in composition. These defects are thought to be responsible for the presence of two distinct types of antiferromagnetic ordering.

1. Introduction

The chemical flexibility of the perovskite structure is well-established. The basic formulation ABO_3, where A is usually a relatively-large divalent or trivalent cation and B is a smaller cation from the d block or p block, must often be changed to $(A_{2-x}A'_x)BB'O_6$ or $(A_{3-x}A'_x)B_2B'O_9$ to show the presence of more than one type of cation on either the A site or the B site, or both. When the A sites, 12-coordinate in the aristotype cubic structure, are occupied by more than one type of cation, the different cations, A and A', are usually distributed in a disordered manner. However, when the six-coordinate B sites are occupied by multiple cation species the different cations, B and B', often occupy the octahedral sites in an ordered manner [1–3]. The degree of ordering is largely determined by the difference in size and charge of the two cations and it in turn often determines the properties of the compound. For example, Sr_2FeTaO_6 has a disordered distribution of Fe^{3+} and Ta^{5+} over the B sites and behaves as a spin glass below 23 K [4], whereas Sr_2FeIrO_6 has nearly complete 1:1 checkerboard ordering of Fe^{3+} and Ir^{5+} (see Fig. 1) and orders antiferromagnetically at 120 K [5]. This is not the only type of cation ordering observed, but it is the most common. Perhaps surprisingly, it is even found in compounds where it is apparently incompatible with the concentration ratio of the two species, for example $La_3Ni_2SbO_9$ [6]. In this case one set of sites in the checkerboard is occupied entirely by Ni^{2+} while the other is occupied by a disordered 1:2 distribution of Ni^{2+} and Sb^{5+}. Fig. 2 shows the arrangement of the B-site cations in a (001) sheet. The presence of antiferromagnetic ordering below 275 K in $KNiF_3$ [7] suggests that there will be strong antiferromagnetic coupling between nearest-neighbour Ni^{2+} cations in this non-frustrated array and, because of the 3:1 imbalance between the number of these cations on the spin-up and spin-down sublattices, this might be expected to result in ferrimagnetism. Consistent with this, the magnetisation of $La_3Ni_2SbO_9$ increases markedly on cooling below 105 K and measurements of the magnetisation at 5 K found a value in excess of 1.5 μ_B per formula unit. However, neutron diffraction experiments detected little or no magnetic Bragg scattering at 5 K [6]. In order to account for this apparent contradiction it was proposed that ferrimagnetic domains exist, but that they are too small to give rise to Bragg scattering. Support for this hypothesis was provided by neutron diffraction experiments carried out in an applied field. The field apparently brought different domains into alignment, thus increasing the coherence length of the magnetic order and enhanced Bragg scattering was observed [8]. The presence of small magnetic domains was attributed to variations in the Ni/Sb concentration which might be expected to increase the relative significance of next-nearest-neighbour superexchange interactions and hence disrupt the long-range magnetic structure. Evidence for

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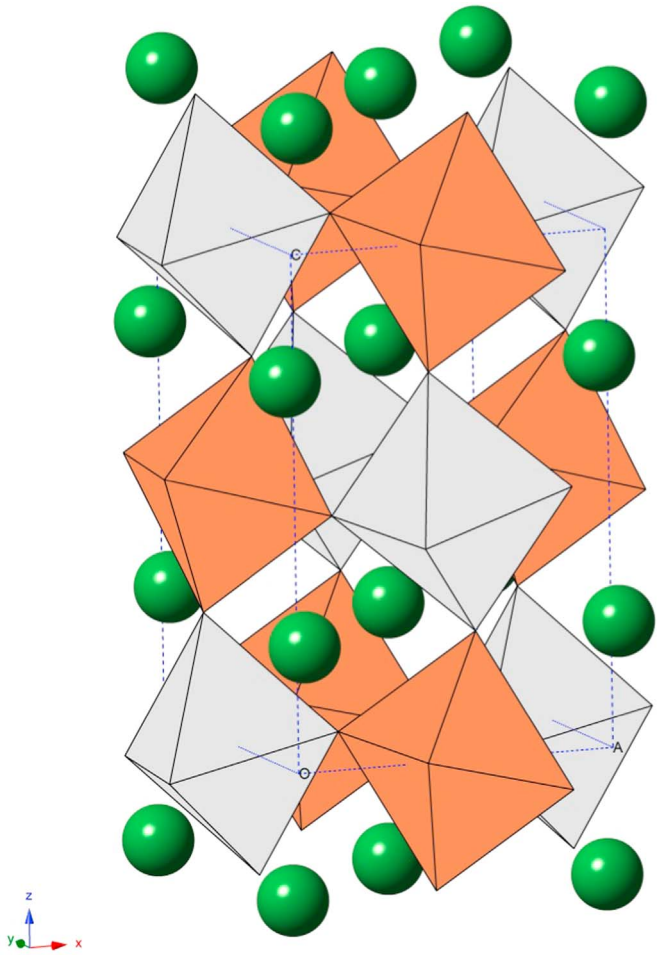

Fig. 1. 1:1 Checkerboard cation ordering in the $A_2BB'O_6$ perovskite structure. Orange and grey octahedra are occupied by *B* and *B′* cations, respectively. The *A* cations are represented by green circles. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

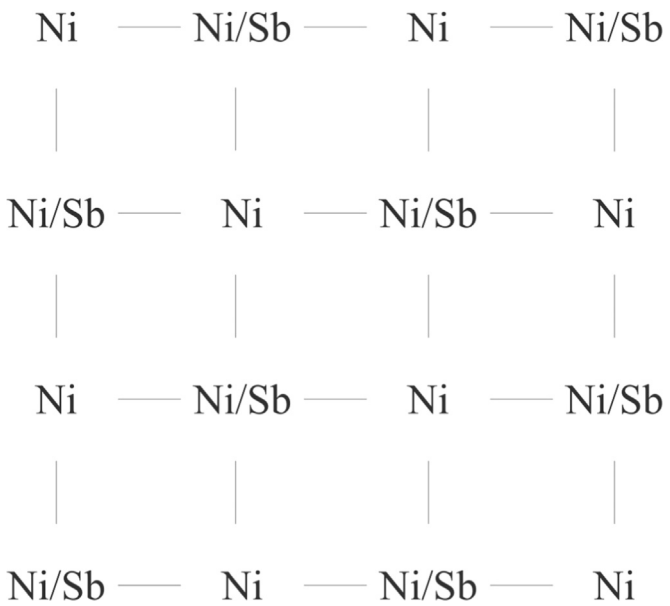

Fig. 2. A 4 × 4 grid illustrating the cation ordering over the B sites of $La_3Ni_2SbO_9$; one set of sites is occupied by Ni^{2+} only, whereas the other set has a 2:1 concentration ratio of Sb^{5+} and Ni^{2+} (represented by the symbol Ni/Sb).

such variations in the Ni/Sb distribution and the consequent disruption of the cation ordering was provided by high-resolution transmission electron microscopy [8]. Overall, the magnetic behaviour of $La_3Ni_2SbO_9$, that is the enhanced susceptibility associated with local ferrimagnetism but in the absence of long-range order detectable in a diffraction experiment, was deemed to be analogous to the electrical behaviour of relaxor ferroelectrics [9], for example $Pb_3MgNb_2O_9$ [10], and $La_3Ni_2SbO_9$ was consequently described as a relaxor ferromagnet. The formula $(A_{3-x}A'_x)B_2B'O_9$, where *B* is a paramagnetic cation and *B'* is diamagnetic, can be satisfied in many different ways and we have therefore begun a program to synthesize more of these oxides in order to identify further examples of relaxor ferromagnetism and to establish the circumstances under which this behaviour occurs. In this paper we describe the synthesis and characterisation of $SrLa_2Ni_2TeO_9$. The two principal differences between this compound and $La_3Ni_2SbO_9$ are that Sb^{5+} has been replaced by the smaller Te^{6+} cation, thus lowering the energy of the valence-shell orbitals of the diamagnetic cation, and that the A sites are now occupied by two cations having different charges. We describe below the consequences of these changes for the magnetic properties of the compound.

2. Experimental

A polycrystalline sample of $SrLa_2Ni_2TeO_9$ was synthesized using the traditional ceramic method. Stoichiometric quantities of $SrCO_3$, NiO, TeO_2 and pre-dried La_2O_3 were initially mixed, ground together and fired in an alumina crucible at 800 °C. The reaction mixture was then pelletised before being heated at 950, 1100, 1200 and finally at 1225 °C, with intermediate regrinding. After a total of six days at 1225 °C the reaction product was cooled to 800 °C in the furnace and then quenched to room temperature.

X-ray powder diffraction data were collected over the angular range $5 \leq 2\theta/^\circ \leq 125$ on a PANalytical Empyrean diffractometer operating with Cu $K_{\alpha 1}$ radiation ($\lambda = 1.54051$ Å) at room temperature. The data were analysed using the Rietveld method [11], as implemented in the GSAS program suite [12], in order to determine the unit cell parameters. Neutron powder diffraction data were collected in angular steps of $\Delta 2\theta = 0.05^\circ$ for $0 \leq 2\theta/^\circ \leq 150$ at room temperature, 50 K and 5 K using the instrument D2b at ILL, Grenoble, France. The sample was held in a vanadium can which was mounted in a Displex refrigerator during the data collection at 5 K. These data were fully analysed using the Rietveld method. A pseudo-Voigt function [13] was employed to model the peak shapes and the background was modelled using an 18-term shifted Chebyshev function. In the analysis of the data collected at room temperature, the unit cell parameters were held at the values determined from the X-ray diffraction data and thus the neutron wavelength was determined to be $\lambda = 1.5937$ Å. Further data sets were collected at temperatures of 5 and 50 K on the diffractometer D1b using a wavelength $\lambda = 2.5238$ Å. D1b has a higher neutron flux than D2b and data from this instrument were used to search for weak Bragg peaks that might go unnoticed on D2b.

Specimens for electron microscopy were prepared by dispersing crushed $SrLa_2Ni_2TeO_9$ powder in ethanol and depositing a few drops of this solution on a copper grid covered with a holey carbon film. Selected-area electron diffraction patterns were recorded with a Philips CM20 transmission electron microscope. High-resolution HAADF–STEM images and atomic resolution STEM-EDX maps were collected with a FEI Titan 80–300 “cubed” transmission electron microscope equipped with a Super-X detector and operated at 300 kV.

The temperature dependence of the dc molar magnetic susceptibility of $SrLa_2Ni_2TeO_9$ was measured using a SQUID magnetometer. Measurements were made while warming the sample