



# Structural and magnetic study of $\text{Yb}^{3+}$ in the perovskites $\text{Sr}_2\text{YbMO}_6$ ( $M = \text{Nb, Ta, Sb}$ )



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## ABSTRACT

The compounds  $\text{Sr}_2\text{YbNbO}_6$ ,  $\text{Sr}_2\text{YbTaO}_6$  and  $\text{Sr}_2\text{YbSbO}_6$  have been prepared using solid state methods by heating pelleted reagents in air at temperatures up to 1400 °C. Rietveld refinement against room temperature neutron powder diffraction data show that all three compounds crystallise with a cation-ordered variant of the perovskite structure in the  $P2_1/n$  space group. Complete cation ordering occurs between  $M^{5+}$  and  $\text{Yb}^{3+}$  over two octahedrally-coordinated sites in the structure and all compounds are stoichiometric in oxygen. The Sb–O bond lengths are similar to related perovskite compounds but differ slightly from those indicated by bond valence sums. Magnetic susceptibility data resemble Curie–Weiss paramagnetic behaviour, but can be better understood as arising from the effect of the octahedral crystal field on the  $^2F_{5/2}$  ground state of  $\text{Yb}^{3+}$  leading to a temperature dependent magnetic moment on this ion below 100 K.

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## 1. Introduction

The perovskite structure undergoes a large number of distortions that allow the accommodation of considerable variation in cation sizes and charges [1]. In addition, when two cations of sufficient difference in size and/or charge occupy the octahedrally-coordinated sites in the structure then cation ordering may also occur. The most common form of ordering leads to an alternating arrangement of cations on these sites and so results in a rock-salt type face-centred cubic (*fcc*) substructure. There is considerable interest in such cation ordering as the *fcc* lattice contains nearest neighbouring cations arranged on regular edge-sharing tetrahedral [2–5]. Consequently antiferromagnetic interactions between moments on these lattice points cannot be satisfied by any collinear ordering in a long-range ordered antiferromagnetic structure. Instead a number of exotic magnetic states exist at low temperatures [6–10]. Interest has mainly focussed on magnetic ions where the unpaired electrons reside in the *d*-orbitals in order to give relatively strong superexchange interactions between the sites of the *fcc* lattice.

A number of cation-ordered perovskites have used lanthanide  $\text{Ln}^{3+}$  ordering with  $\text{Mo}^{5+}$  to access a range of physical behaviour. For the larger lanthanides the structure is tetragonally distorted at

higher temperatures due to  $\text{Ba}^{2+}$  being too small to match the Goldschmidt radius for a cubic perovskite [11]. Both  $\text{Ba}_2\text{NdMoO}_6$  and  $\text{Ba}_2\text{SmMoO}_6$  exhibit a distortion of the  $\text{MoO}_6$  octahedra with two short Mo–O and four longer Mo–O bonds that partially stabilise the  $4d^1$  electronic configuration [11,12].  $\text{Ba}_2\text{GdMoO}_6$  undergoes a transition from cubic to tetragonal symmetry at 220 K before undergoing a ferroelastic distortion to a triclinically-distorted phase at 80 K [13]. For the smaller lanthanides the compounds exhibit the undistorted face-centred cubic structure [11]. Where  $\text{Ln}^{3+}$  is a diamagnetic cation such as  $\text{Y}^{3+}$  or  $\text{Lu}^{3+}$  this gives a face-centred array of  $4d^1 \text{Mo}^{5+}$  cations with no other paramagnetic species present in the compound [10,11]. Antiferromagnetic coupling between nearest neighbours on such a lattice leads to geometric frustration due to the formation of regular tetrahedra of mutual interactions that cannot be simultaneously satisfied.

The antiferromagnetic coupling in the series  $\text{Ba}_2\text{LnMoO}_6$  shows a large variation in magnitude from ca. –130 to –8 K.  $\text{Ba}_2\text{YMoO}_6$  [8–9,11] and  $\text{Ba}_2\text{LuMoO}_6$  [10] show strong coupling with Weiss constants of ca. –130 K but the formation of a long range antiferromagnetically ordered state is suppressed due to the frustrated *fcc* lattice [11]. Instead, a loss of the bulk magnetic moment is observed on cooling along with a reduction in the electronic entropy and a Knight shift in the  $^{89}\text{Y}$  NMR suggesting [8–9] that this arises from the formation of a valence bond state. This assignment has been confirmed by the observation of an excitation from the  $S = 1/2$  spin singlet ground state in  $\text{Ba}_2\text{YMoO}_6$  [14]. The paramagnetic species  $\text{Er}^{3+}$  has a similar size to the diamagnetic cations  $\text{Y}^{3+}$  and  $\text{Lu}^{3+}$ , and  $\text{Ba}_2\text{ErMoO}_6$  has the same cubic structure, but shows only weak

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antiferromagnetic coupling with a Weiss constant  $\approx -10$  K [15]. This can be contrasted with the isostructural compound  $\text{Ba}_2\text{YbMoO}_6$  which has a Weiss constant that is an order of magnitude larger,  $-116$  K [11].

The variation in physical behaviour from valence bond glass, to ferroelastic phase transitions, to Jahn–Teller distortions provide strong evidence that subtle variations in the chemistry of the  $\text{Ln}^{3+}$  bonding have an important impact on the physical properties of the series  $\text{Ba}_2\text{LnMoO}_6$ . The effect of the crystal field on lanthanide cations can be significant at very low temperature, as shown in  $\text{Ba}_2\text{HoSbO}_6$ , but even in this case the magnetic behaviour at high temperature suggests Curie–Weiss paramagnetism with weak ( $\theta = -7.7$  K) antiferromagnetic coupling between  $\text{Ho}^{3+}$  cations [6].

We have examined the role of the  $4f$  orbitals in these systems by preparing diamagnetic analogues of the  $\text{Mo}^{5+}$  compounds. Here we report three compounds where the only paramagnetic species is the  $\text{Yb}^{3+}$  cation and so examine the magnetic interactions between  $\text{Yb}^{3+}$  cations occupying the points of the distorted  $fcc$  lattice shown in Fig. 1. Neutron diffraction has been used to accurately determine the structure of three new compounds, and a Curie–Weiss analysis of the magnetic susceptibility would suggest surprisingly strong interactions between the  $4f^{13}$  centres. Here, we show that the magnetic susceptibility can better be explained by the subtle effect of the crystal field on the isolated  $4f$  orbitals.

## 2. Experimental

Polycrystalline samples were prepared from stoichiometric mixtures of reagents using conventional solid state methods. All reagents had a purity of not less than 99.99%. Strontium carbonate, ytterbium oxide and niobium–tantalum- or antimony(V) oxide were ground in a mortar and pestle and then pressed into pellets of 13 mm diameter under a load of ca. 2 t. The pellets were then heated at  $800^\circ\text{C}$  for 1 day. The samples were then ground, repelleted and heated in air at a number of temperatures increasing up to  $1400^\circ\text{C}$ . Due to the slow rate of product formation the samples were reground up to ten times and

the total heating times amounted to around 30 days. Alternative sol gel preparations [16] gave an initially more rapid product formation but did not achieve a pure sample any more rapidly than the conventional ceramic route.

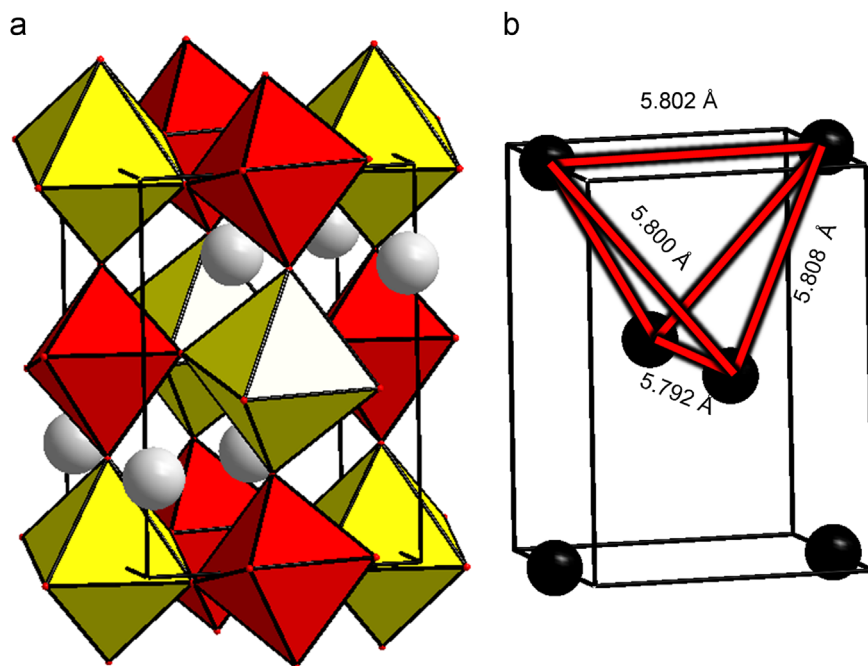
X-ray powder diffraction was used to follow the progress of the reaction. Data were collected in Bragg Brentano geometry using a Panalytical Xpert diffractometer operating with  $\text{CuK}\alpha$  radiation.

Neutron diffraction data were collected using the time-of-flight high-resolution powder diffractometer (HRPD) at the ISIS spallation source at the Rutherford Appleton Laboratories, Didcot, UK. For these experiments ca. 5 g of sample was contained in a cylindrical vanadium can, with an internal diameter of 11 mm. Diffraction patterns were recorded over the time-of-flight range 30–130 ms in back-scattering and  $90^\circ$  detector banks, in order to sample a  $d$ -spacing range from 0.6 to 3.9 Å. Data analysis used the Rietveld method [17] of structure refinement as implemented in the GSAS suite of programs [18,19]. Refinements were carried out simultaneously against both banks of data. An empirical fit to the background was carried out using shifted Chebyshev functions and a convolution of exponential and pseudo Voigt functions was used to model the profile of the Bragg peaks.

Magnetic data were collected using a Quantum Design SQUID magnetometer. Around 100 mg of each sample was accurately weighed into gelatin capsules and data were recorded after cooling the samples in either the measuring field of 100, 1000 or 5000 G or zero applied field. Data were corrected for diamagnetism of the sample, but this had no significant effect on the size of the susceptibility. Bond valence sums were determined using the parameters derived from a library of metal oxides [20].

## 3. Results

X-ray powder diffraction data collected from each of the three compositions contained the peaks associated with the primitive perovskite structure with lattice parameter  $a_p \approx 4.1$  Å, but showed additional reflections and peak splitting indicative of cation-ordering



**Fig. 1.** (a) The cation-ordered perovskite structure exhibited by  $\text{Sr}_2\text{YbMO}_6$ . Grey spheres show  $\text{Sr}^{2+}$  cations whilst yellow and red octahedra represent  $\text{YbO}_6$  and  $\text{Nb/Ta/SbO}_6$  units respectively. The distortion from cubic symmetry lifts the degeneracy of the pseudo face-centred cubic ( $fcc$ ) lattice of  $\text{Yb}^{3+}$  centres, although as indicated by the distances shown in (b) the tilting of the octahedra leads to minimal distortion in the tetrahedra that compose the pseudo- $fcc$  lattice. The pseudo- $fcc$  lattice is composed of  $\text{Yb}^{3+}$  centres as indicated by black spheres in (b). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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