Materials Research Bulletin 98 (2018) 173–179

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Magnetic properties of monoclinic lanthanide orthoborates, $LnBO_3$, Ln = Gd, Tb, Dy, Ho, Er, Yb

P. Mukherjee[a,*], Y. Wu[a], G.I. Lampronti[b], S.E. Dutton[a]

[a] Cavendish Laboratory, University of Cambridge, JJ Thomson Avenue, Cambridge CB3 0HE, United Kingdom
[b] Department of Earth Sciences, Downing Site, University of Cambridge, Downing Street, Cambridge CB2 3EQ, United Kingdom

ARTICLE INFO

Keywords:
A. Inorganic compounds
B. Magnetic properties
C. X-Ray diffraction
D. Crystal structure
D. Specific heat

ABSTRACT

The lanthanide orthoborates, $LnBO_3$, Ln = Gd, Tb, Dy, Ho, Er, Yb crystallise in a monoclinic structure with the magnetic Ln^{3+} forming an edge-sharing triangular lattice. The triangles are scalene, however all deviations from the ideal equilateral geometry are less than 1.5%. The bulk magnetic properties are studied using magnetic susceptibility, specific heat and isothermal magnetisation measurements. Heat capacity measurements show ordering features at $T \leq 2$ K for Ln = Gd, Tb, Dy, Er. No ordering is observed for $YbBO_3$ at $T \geq 0.4$ K and $HoBO_3$ is proposed to have a non-magnetic singlet state. Isothermal magnetisation measurements indicate isotropic Gd^{3+} spins and strong single-ion anisotropy for the other Ln^{3+}. The change in magnetic entropy has been evaluated to determine the magnetocaloric effect in these materials. $GdBO_3$ and $DyBO_3$ are found to be competitive magnetocaloric materials in the liquid helium temperature regime.

1. Introduction

Materials having magnetic lattices with triangular or tetrahedral geometries are often frustrated due to the inability of all the pairwise interactions to be satisfied simultaneously. For a particular frustrated plaquette, the magnetic properties vary widely because factors including crystal electric field (CEF) effects and lattice distortions compete with the magnetic interactions to determine the magnetic ground state. Depending on the relative magnitudes of such interactions, exotic ground states may emerge. Realisation of such states in real materials open up the possibility of testing theoretical predictions and realisation of novel magnetic properties [1–3].

There have been many studies on three-dimensional (3D) frustrated lattices containing magnetic Ln^{3+} ions; most notably the pyrochlores – $Ln_2B_2O_7$ (B = Ti, Sn) and more recently $Ln_2Zr_2O_7$ but also other materials including gadolinium gallium garnet (GGG) and the $SrLn_2O_4$ family of materials [4–11]. Work on two-dimensional (2D) frustrated lattices containing magnetic Ln^{3+} has been limited due to the lack of experimental realisations [12], however this field is gaining momentum. Recently the isostructural series $Ln_3X_2Sb_3O_{14}$ (X = Mg, Zn) have been reported which contain structurally perfect 2D kagome planes of magnetic Ln^{3+} [13–15]. Several exotic ground states have been already reported including umbrella-like all-in all-out long range ordering for $Nd_3Mg_2Sb_3O_{14}$, dipolar interaction mediated long-range ordering in a 120° structure for $Gd_3X_2Sb_3O_{14}$ (X = Mg, Zn), emergent charge order in $Dy_3Mg_2Sb_3O_{14}$ and a possible Kosterlitz-Thouless (KT) vortex unbinding transition in $Er_3Mg_2Sb_3O_{14}$ [16–18]. Another recent discovery is the Quantum Spin Liquid (QSL) candidate $YbMgGaO_4$ where the magnetic Yb^{3+} with effective spin S = ½ form a triangular lattice. Bulk magnetic measurements in this material shows no evidence of ordering down to 60 mK while neutron scattering experiments have revealed a continuum of magnetic excitations, consistent with a QSL state [18,19]. The bulk magnetic properties of the $KBaLn(BO_3)_2$ series, which crystallise in a structure containing edge-sharing triangular lattices of Ln^{3+}, have also been recently reported [20]. Discovery of other 2D frustrated lattices with magnetic rare earth ions opens up the possibility of exploring further aspects of 2D geometrically frustrated systems.

Lanthanide orthoborates, $LnBO_3$, have been widely studied for their optical properties because they have high ultraviolet transparency and high optical damage thresholds, making them suitable for applications as phosphors in vacuum discharge lamps and screens [21–23]. However, except for early studies on magnetic susceptibility [24,25], their magnetic properties have not been explored. The synthesis and crystal structure of the $LnBO_3$ was first reported by Levin et. al. [26]. It was proposed that the lanthanide orthoborates $LnBO_3$ crystallise in the same three structures as $CaCO_3$ depending on the Ln^{3+} ion – aragonite for the larger Ln^{3+} (La – Nd), vaterite for the smaller Ln^{3+} (Eu – Yb) and calcite for the smallest Ln^{3+} ion, Lu. $SmBO_3$ was reported to crystallise in the vaterite phase between 1100 and 1300 °C and in a different

* Corresponding author.
E-mail address: pm545@cam.ac.uk (P. Mukherjee).

http://dx.doi.org/10.1016/j.materresbull.2017.10.007
Received 3 July 2017; Accepted 4 October 2017
Available online 13 October 2017

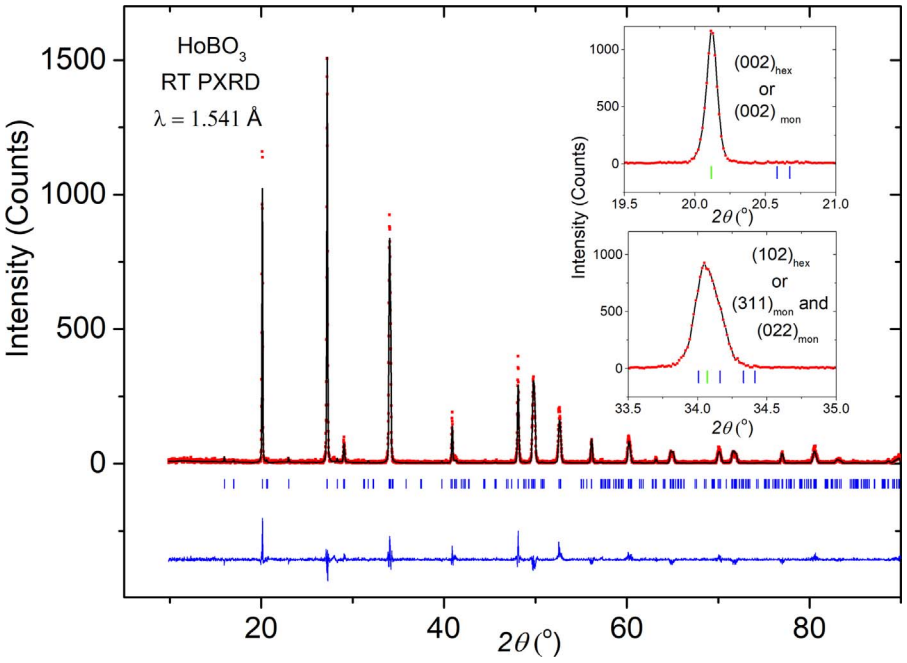

Fig. 1. PXRD pattern for $HoBO_3$: Experimental data (red dots), Modelled data (black line), Difference pattern (blue line), Bragg positions (blue ticks, reflections for hexagonal setting are highlighted in green); Inset: Peaks at 20.1° and 34.1°. Peak at ~20.1° corresponds to single reflection in both hexagonal $(002)_{hex}$ and monoclinic setting, $(002)_{mon}$. Peak at ~34.1° corresponds to single reflection in hexagonal setting, $(102)_{hex}$, but two reflections in monoclinic setting, $(311)_{mon}$ and $(022)_{mon}$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Crystal structure parameters for monoclinic $LnBO_3$ - space group $C2/c$: $Ln1$ occupies the 4c site (0.25, 0.25, 0), $Ln2$ occupies the general 8f (x, y, z) site. The $Ln2$ positions were refined from the PXRD data. All the B and O positions were kept fixed as follows: B1 occupies the general 8f (x, y, z) site = (0.12011, 0.03790, 0.24691) while B2 occupies the 4e site (0,y, 0.25) = (0, 0.67520, 0.25). O1, O2, O3, O4 all occupy the general 8f (x, y, z) positions; O1 = (0.12550, 0.09200, 0.10199), O2 = (0.22293, 0.09316, 0.38870), O3 = (0.04837, 0.56643, 0.39233), O4 = (0.39142, 0.30823, 0.25174) while O5 occupies the 4e site (0, y, 0.25) = (0, 0.135, 0.25). The values of thermal parameters were kept fixed at B_{iso} = 0.8 Å^2 for all atoms.

Ln		Gd	Tb	Dy	Ho	Er	Yb
a (Å)		11.4968(6)	11.4299(4)	11.3755(3)	11.3357(4)	11.2911(3)	11.2006(2)
b (Å)		6.6402(3)	6.6037(2)	6.5757(3)	6.5502(2)	6.5236(2)	6.47250(14)
c (Å)		9.6796(4)	9.6408(2)	9.6092(3)	9.5776(2)	9.5475(2)	9.4901(2)
β (Å)		113.048(5)	112.945(2)	112.919(2)	112.930(2)	112.914(2)	112.8116(2)
Volume (Å^3)		679.96(6)	670.11(3)	662.04(4)	654.95(3)	647.76(2)	634.18(2)
χ^2		1.12	1.04	1.39	1.55	1.54	1.41
Ln2: 8*f* (x,y,z)	x	0.0816(15)	0.0811(8)	0.0826(12)	0.0819(6)	0.0851(3)	0.0839(4)
	y	0.25282(19)	0.25387(8)	0.25351(10)	0.25405(5)	0.25280(5)	0.25346(5)
	z	0.49251(13)	0.49894(11)	0.49614(14)	0.49743(8)	0.50038(6)	0.49993(6)

triclinic structure at other temperatures. Since then, there has been much debate about the crystal structure of the so-called π-$LnBO_3$, Ln = Eu − Yb, with later studies proposing the existence of both a hexagonal or 'pseudo-vaterite' [22,27] and monoclinic structure [23,28,29]. However, in both the proposed structures, the magnetic Ln^{3+} link to form edge-sharing triangles and thus, the π-$LnBO_3$ may be an example of a new series of geometrically frustrated magnetic materials containing Ln^{3+}.

In this paper we report the synthesis, characterisation and bulk magnetic properties on polycrystalline samples of $LnBO_3$, Ln = Gd, Tb, Dy, Ho, Er and Yb. The materials have been prepared by solid state synthesis and the crystal structure analysed using powder X-Ray diffraction (PXRD). The bulk magnetic properties have been studied using magnetic susceptibility, heat capacity and isothermal magnetisation measurements. To the best of our knowledge, this is the first comprehensive report on the magnetic properties. The $LnBO_3$ exhibit different magnetic ordering features, the magnetic behaviour is highly dependent on the Ln^{3+} under consideration. Evaluation of the magnetocaloric effect shows that $GdBO_3$ and $DyBO_3$ are competitive materials for solid state magnetic refrigeration in the liquid helium temperature regime, $T \geq 2$ K.

2. Experimental section

Samples of $LnBO_3$, Ln = Gd, Tb, Dy, Ho, Er and Yb, were prepared using a solid-state synthesis method. Gd_2O_3 was pre-dried at 800 °C overnight prior to being weighed out to ensure the correct stoichiometry. Samples were prepared by mixing stoichiometric amounts of Ln_2O_3 (Ln = Gd, Dy, Ho, Er, Yb) or Tb_4O_7 and H_3BO_3 (5% excess to compensate for the loss of B due to volatilisation during heating). A pre-reaction was carried out at 350 °C for 2 h to decompose the H_3BO_3 to B_2O_3. After regrinding, samples were heated to 1000 °C for either 24 or 48 h to obtain the final product.

The formation of a phase pure product was confirmed using room temperature (RT) powder X-Ray diffraction (PXRD). Initially short scans were collected over 5° ≤ 2θ ≤ 60° (Δ 2θ = 0.015°) using a Panalytical Empyrean X-Ray diffractometer (Cu Kα radiation, λ = 1.541 Å). For more detailed structural analysis, longer scans at high resolution were collected using a Bruker D8 Advance diffractometer (Cu Kα radiation, λ = 1.541 Å, Ge monochromator and Sol-XE energy dispersive detector). Measurements were carried out for a day over an angular range 10° ≤ 2θ ≤ 120° (Δ 2θ = 0.01°). Rietveld refinement was carried out using the Fullprof suite of programs [30]. The backgrounds were fitted using linear interpolation and the peak shape was modelled using a pseudo-Voigt function.

Magnetic susceptibility measurements were performed on a Quantum Design Magnetic Properties Measurement System (MPMS) with a Superconducting Quantum Interference Device (SQUID) magnetometer. The zero-field cooled (ZFC) susceptibility $\chi(T)$ was measured in a field of 100 Oe in the temperature range 2–300 K. In a field of