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# Single crystal growth by the floating-zone method of a geometrically frustrated pyrochlore antiferromagnet, $Tb_2Ti_2O_7$

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**Abstract**

Large, high quality, single crystals of $Tb_2Ti_2O_7$, have been successfully grown by the floating zone method under a controlled atmosphere. Crystals, approximately 3–5 mm in diameter and up to 20 mm in length, were grown from a small seed crystal. Several crystals have been characterised to determine their crystal quality, chemical structure and magnetic properties and these results were compared to those of sintered polycrystalline pellets. These materials were shown to have the face centred cubic structure, Fd–3m, with a room temperature lattice parameter $a = 10.12(7)$ Å, when grown in oxygen, and $a = 10.13(6)$ Å, when grown in argon. They are currently of interest as they are comprised of antiferromagnetically coupled magnetic moments residing on a network of corner-sharing tetrahedra, a system known to display the effects of geometrical frustration. Magnetic susceptibility measurements, with the applied field parallel to the growth direction were performed on both crystals. Both single crystal and polycrystalline samples showed very similar Curie-Weiss like behaviour down to 5 K, with Curie–Weiss temperatures, $\theta_{cw}$ of approximately $-19$ K. 

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## 1. Introduction

The combination of a triangle-based lattice symmetry and antiferromagnetism results in phenomena known as geometrical frustration, which has recently attracted much interest [1–7]. Frustration is the inability of a system to simultaneously minimize the total energy of its classical ground state by minimizing individual microscopic interactions. It is relatively easy to understand the origin of frustration in the classic geometrically frustrated lattice, a triangular lattice with antiferromagnetic

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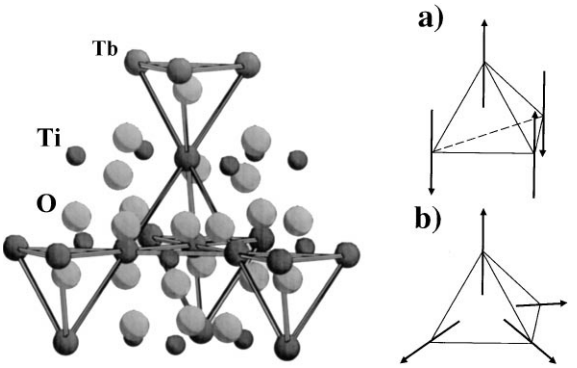


Fig. 1. A schematic of the $Tb^{3+}$ tetrahedral structure and its local environment. Insets (a) and (b) illustrate frustration and a possible ordered phase, respectively, on a tetrahedral lattice.

nearest-neighbour interaction, for which two neighbouring moments can align in a spin-up–spin-down arrangement but the third cannot satisfy both its nearest neighbours at any one time. In the tetrahedral coordination, two antiferromagnetic bonds are always broken, when the other four are satisfied (see Fig. 1a). The ground state of these systems is seen to be highly degenerate which is a general feature of frustrated magnetic systems. Fig. 1b shows a tetrahedral lattice where the total energy has been minimised by aligning the magnetic moments at 109° to each other, thus forming a noncollinear structure.

The oxide pyrochlore family, with chemical composition $A_2B_2O_7$, crystallises into a face centred cubic structure with eight formula units per conventional unit cell [1]. The A and B metal atoms form two infinite networks of corner sharing tetrahedra. If the A and/or B atom is magnetic, with an antiferromagnetic nearest neighbour interaction, then a high degree of frustration must exist within the lattice. In $Tb_2Ti_2O_7$ only the $Tb^{3+}$ (A) site is magnetic. It is located on the 16d site and the identical tetrahedral sublattice of nonmagnetic Ti is displaced by (1/2, 1/2, 1/2) onto the 16c site of the Fd–3m space group. The trivalent rare-earth ion has eightfold oxygen coordination, producing a puckered hexagon structure and the Ti ion has sixfold oxygen coordination. Fig. 1 shows the tetrahedral structure of the Tb sublattice and its local environment.

A recent study on polycrystalline $Tb_2Ti_2O_7$ [3] has shown that the system does not display conventional Néel order or a glass-like state, unlike the majority of known frustrated magnetic systems, down to 0.05 K, despite the fact that antiferromagnetic correlations develop at $\approx 50$ K. $Tb_2Ti_2O_7$ is thus believed to be a cooperative paramagnet, a term coined by Villain [4] to describe such a low temperature state.

Until recently, only small oxide pyrochlore crystals have been available to the scientific community. These crystals were usually grown using a flux-melt [5] or a high-temperature melt technique [6]. The growth of many of the oxide pyrochlores has thus been hindered by contamination with the crucible material and/or the high melting temperatures of these materials. The floating zone (FZ) technique is one of the most useful methods for synthesising oxide single crystals [8,9]. One advantage of this technique is that there is no contamination from a containment vessel, as none is used. Other advantages are the relatively high-temperatures attainable ($<2800$°C) and that the crystals produced are usually easily separated from the bulk and have flux-free surfaces.

In this paper we will report on the crystal growth of $Tb_2Ti_2O_7$ using the floating zone technique. The crystals have been characterised and we compare these results with those obtained from polycrystalline material.

## 2. Experimental details

Polycrystalline samples of $Tb_2Ti_2O_7$ were prepared by firing, in air, stoichiometric amounts of high purity ($>99.99\%$) $Tb_2O_3$ and $TiO_2$ for several days with intermittent grindings to ensure a complete reaction. The resulting stoichiometric powder was moulded into cylindrical rods approximately 70 mm in length with a uniform radius of about 5 mm. This was achieved with a sealed rubber tube, filled evenly with powder and pressed for 5 min at approximately 200 kg/cm$^2$ in a cold isostatic press. The polycrystalline rods were then sintered at 1350°C, in air, for 12 h. The resulting sintered rods were approximately 75% of the theoretical density and used as feed rods in the image furnace.

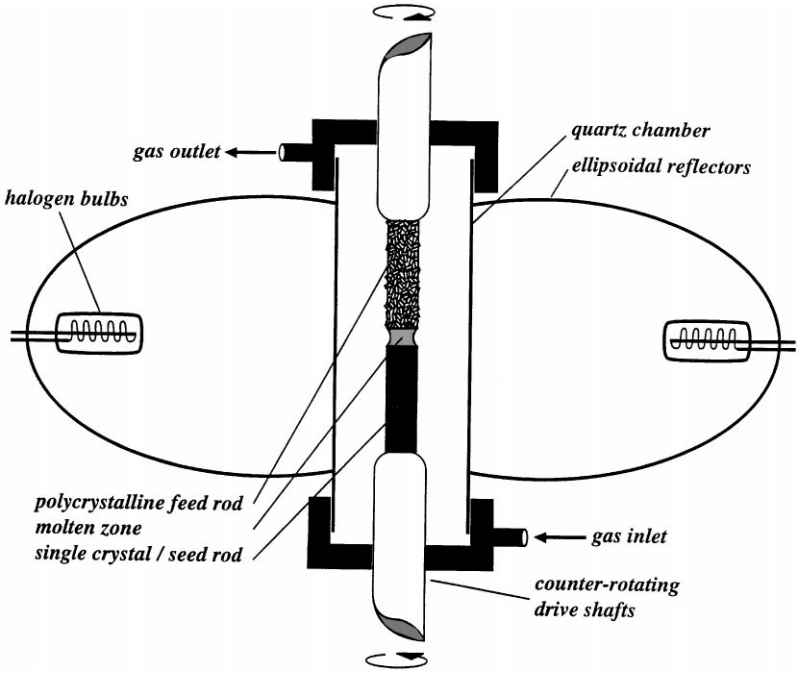


Fig. 2. A schematic diagram of the Infra-red image furnace used in this study. The high attainable temperatures and the lack of a containment vessel makes this an ideal method for growing high-quality crystals.

The crystal growth experiments were carried out by the FZ technique using a double ellipsoid image furnace (NEC SC-N35HD) at the University of Warwick, UK. A schematic of the furnace is shown in Fig. 2. The infrared radiation source used was two 3.5 kW halogen lamps. The molten zone was established between a polycrystalline feed rod and a small single crystal seed rod (from a previous growth, for which the melt was contained between two polycrystalline rods). The seed and feed rods were counter-rotated between 10 and 20 rpm and moved through the hot zone at 5–20 mm/h. The growth was carried out under an over pressure of either oxygen or argon with a flow rate of 200 ml/min.

The samples obtained were characterized by means of X-ray diffraction and magnetic susceptibility. Static susceptibility measurements were carried out between 2 K and room temperature in a high field Quantum Design SQUID magnetometer. A Phillips PW2273/20 diffractometer with a Cu target was used for room temperature X-ray diffraction experiments. Neutron diffraction measurements were carried out on the E3 spectrometer of the NRU reactor at Chalk River Laboratories, Canada.

## 3. Results and discussion

Fig. 3 shows the sepia coloured $Tb_2Ti_2O_7$ boule that resulted from one crystal growth in an oxygen

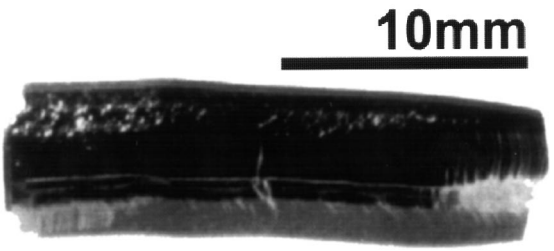


Fig. 3. As-grown $Tb_2Ti_2O_7$ single crystal grown by the floating zone method.

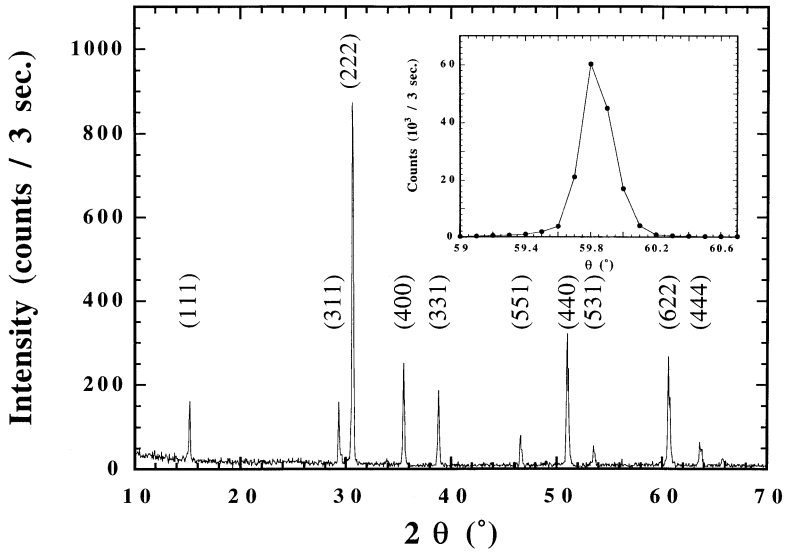


Fig. 4. The room temperature X-ray diffraction pattern from a small piece of the single crystal that was crushed. The inset shows the (4, 4, 0) rocking curve of the single crystal, obtained by neutron diffraction.

atmosphere, using a seed crystal. A small piece of the boule was ground up into a fine powder for a room temperature X-ray diffraction experiment. The diffraction pattern (Fig. 4), can be indexed to the face centered cubic Fd–3m lattice with the lattice parameter, $a = 10.12(7)$ Å, which is in good agreement with the value obtained by Brixner [10] from studies on sintered pellets of $Tb_2Ti_2O_7$. It was shown, by neutron diffraction, that the boule in Fig. 3 consists of two single crystals. One small crystal ($<0.2\ cm^3$) was confined to one end of the boule and was easily masked from the larger crystal. The inset to Fig. 4 shows a rocking curve of the (4, 4, 0) Bragg peak of the large crystal ($\approx 1.3\ cm^3$). It is evident from the narrow width (FWHM $\approx 0.3^\circ$), measured over the length of the crystal ($\approx 20$ mm), that the crystalline quality is very good. Crystals of approximately $0.2\ cm^3$ were also found in boules grown in argon. Room temperature X-ray powder diffraction measurements determined the crystallographic lattice parameter, $a = 10.13(6)$ Å, which is in good agreement with that obtained from polycrystalline samples and crystals grown in oxygen. Neutron diffraction studies showed that the growth direction for all the crystals grown was the $[h, -h, 0]$ direction.

It is worth mentioning that crystals grown in argon were noticeably lighter in colour than those grown in oxygen. Similar changes in colour have been seen in titanium oxide (rutile) crystals, and these are associated with changes in the oxygen stoichiometry, which can be controlled by both temperature and oxygen partial pressure.

Fig. 5 shows the static magnetic susceptibility of polycrystalline $Tb_2Ti_2O_7$ between 2 and 200 K in a small field (100 G). The high-temperature polycrystalline data follows the Curie–Weiss law with a calculated effective magnetic moment of 9.4 $\mu_B$ which is in good agreement with the free ion, $^7F_6$, value of $Tb^{3+}$ of 9.6 $\mu_B$. The Curie–Weiss temperature, also calculated from the high-temperature fit, was found to be $-19$ K. Results from single crystals grown in oxygen and argon are also shown in Fig. 5. The crystals were placed in the magnetometer with the growth direction parallel to the applied field of 100 G. Fitting the results to the Curie–Weiss law gave an effective magnetic moment within experimental error of each other and a slightly higher $\theta_{cw}$ for the crystal grown in

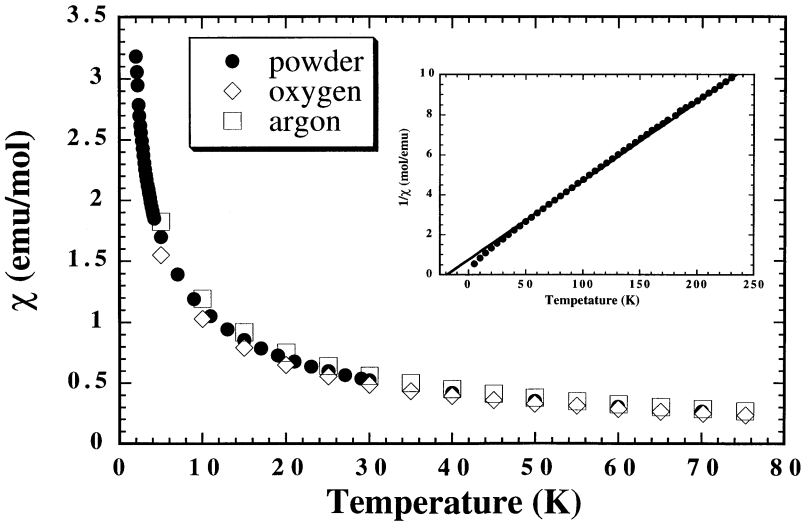


Fig. 5. The temperature dependence of the static susceptibility of $Tb_2Ti_2O_7$ in polycrystalline material and single crystals grown in both a oxygen and argon atmosphere. The high temperature ( > 200 K) fit to the Curie–Weiss law for the polycrystalline sample is shown in the inset.

argon (−23 K) than that grown in oxygen (−18 K).

Below 100 K, the measured susceptibilities begin to deviate from the Curie–Weiss behaviour. This is believed to be due, in part, to the presence of a crystal field level at ≈120 K [3] and the build up of magnetic correlations below this temperature. No cusp or magnetic history dependence was observed in any of the $Tb_2Ti_2O_7$ samples down to 2 K in these small fields. This is consistent with earlier μSR studies [3] on polycrystalline material that concluded that no magnetic transition occurs in small fields down to 0.05 K.

## 4. Conclusions

The floating zone method has been used to produce single crystals of $Tb_2Ti_2O_7$, a geometrically frustrated pyrochlore, that has been shown to remain in its paramagnetic phase down to 0.05 K [3]. Large, high quality, single crystals of $Tb_2Ti_2O_7$, have been successfully grown under a controlled atmosphere, of oxygen or argon, from a seed crystal. Several typical single crystals were characterised by magnetisation and diffraction techniques and they were shown to have similar properties to those already measured in polycrystalline samples.

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