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LETTER TO THE EDITOR

Single crystal growth of rare earth titanate pyrochlores

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Abstract. Rare earth titanate pyrochlores are known to exhibit magnetic frustration. Large, high quality single crystals of a series of oxide pyrochlores, $R_2Ti_2O_7$, have been grown by the floating zone technique, using an infrared image furnace. The crystals are roughly 5–6 mm in diameter and 40–60 mm in length and have been grown for R = Pr, Nd, Sm, Tb, Dy, Ho, Er and Y. The crystals have been characterized and tested for their quality.

Oxides of the type $R_2Ti_2O_7$ (R = rare earth) belong to the family of pyrochlores with a general formula $A_2B_2O_7$. The oxide pyrochlores have a face centred cubic structure, space group $Fd\bar{3}m$. The structure consists of distorted AO_8 cubes and BO_6 octahedra. The metal atoms form a three-dimensional network of corner sharing tetrahedra [1]. In this structure, if either the A or B atom is magnetic, and if the nearest-neighbour interactions are antiferromagnetic, the result is that there is a high degree of frustration in the lattice. The frustrated magnetism in the oxide pyrochlores has been widely investigated using techniques such as magnetic susceptibility and powder neutron diffraction down to low temperatures [2]. Detailed investigations of the magnetic properties and the ground state of the titanate pyrochlores have been hampered by the lack of good quality, sizeable crystals. With the exception of a few investigations on $Ho_2Ti_2O_7$ [3] and $Tm_2Ti_2O_7$ [4] single crystals, most of the literature reports research using powder samples.

Crystals of a few oxide pyrochlores have been grown previously by flux methods [5]. The sizes of the crystals grown by these methods vary, and it is often difficult to obtain crystals large enough in volume, especially for neutron scattering experiments. The 'floating zone' method of crystal growth is ideal for the growth of oxides and almost completely overcomes the problems associated with the conventional methods of crystal growth [6]. This method does not make use of a crucible, thus eliminating contamination problems. The problems associated with the conventional flux growths, where it is difficult to remove the crystals from the molten mass after growth, are also not encountered in this method. The floating zone technique for oxides makes use of an infrared (IR) image furnace, where light from two halogen lamps is brought to a common focus at the sample position by two semi-ellipsoidal mirrors. The sample area is enclosed in a quartz tube, inside which the atmosphere can be maintained at pressures of up to 3–4 atmospheres greater than the ambient pressure with a chosen gas. Temperatures of up to 2150 °C may be achieved at the sample position, which is sufficient to melt most oxides.

In this letter, we report the crystal growth of the pyrochlores, $R_2Ti_2O_7$ where R = Pr, Nd, Sm, Tb, Dy, Ho, Er and Y by the floating zone technique. A previous study [7] has shown the feasibility of this growth technique for producing crystals of one member of

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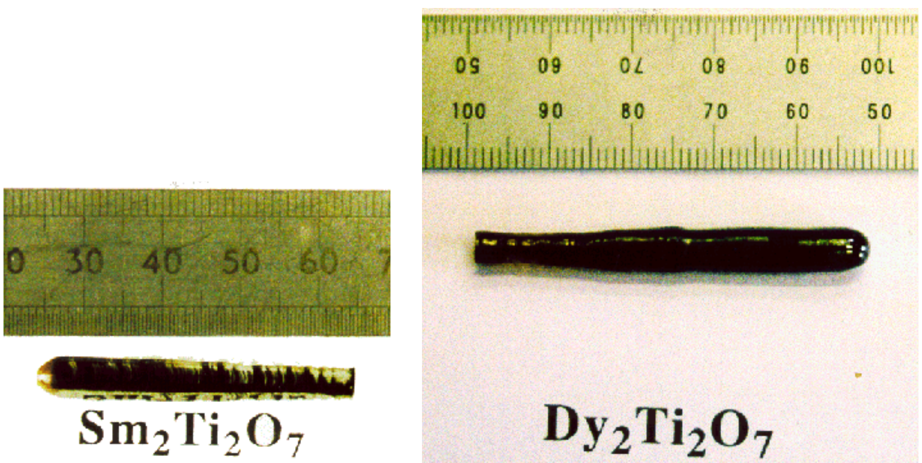
this series, $Tb_2Ti_2O_7$. The present study demonstrates for the first time that large, good quality crystals of the entire series of titanate pyrochlores containing rare earths may be grown using this technique. This is particularly important for the systematic study of the properties of these frustrated magnets as a function of varying the rare earth. The large high quality crystals grown are suitable for most investigations, including those using neutrons as a probe.

The pyrochlores were first synthesized in polycrystalline form by reacting the starting oxides, RE_2O_3 (99.9%) and TiO_2 (99.99%) at 1300 °C in air for several days with intermediate grindings. The powders were then isostatically pressed into rods 6–8 mm in diameter and 60–80 mm long, and sintered at 1350 °C in air. The sintered rods were used for the crystal growth. The crystals were grown using a double ellipsoidal IR image furnace (NEC-N35HD) equipped with two 3.5 kW halogen lamps. A floating molten zone was established between a polycrystalline feed rod, freely suspended from the upper shaft, and a seed rod held at the bottom. Both the feed and the seed rods were counter-rotated at 20–30 rpm to ensure efficient mixing and homogeneity. The rods were then lowered synchronously through the hot zone at speeds of 5–8 mm h^{-1} for crystal growth. Initially, polycrystalline rods were used as seeds and once satisfactory crystals were obtained, a crystal was used as a seed for subsequent growths. The crystals were grown in air, at ambient pressure in all cases.



(a) (b)

Figure 1. Single crystal of (a) $Sm_2Ti_2O_7$ and (b) $Dy_2Ti_2O_7$ grown by the floating zone method, in air, at 6 mm h^{-1}.

Most of the crystals developed facets as they grew and all of them were transparent to light. The colours of the crystals ranged from pink to deep red. Figure 1 shows the photographs of two titanate pyrochlore crystals grown by the floating zone method. The crystals were typically 5 mm in dia and 40 to 60 mm long. Crystals with a maximum diameter of 8–9 mm may be grown by this method. All the Ti-based pyrochlores that we have grown as crystals appear to melt congruently and the crystal growth posed no problems at all. The crystals were characterized by x-ray Laue patterns. The Laue photographs indicate that the crystals grew along the (110) direction in most cases, and in some cases the (110) direction was inclined at ~30 degrees to the growth axis depending on the choice of the seed crystal orientation. An x-ray Laue photograph taken of a crystal of $Sm_2Ti_2O_7$

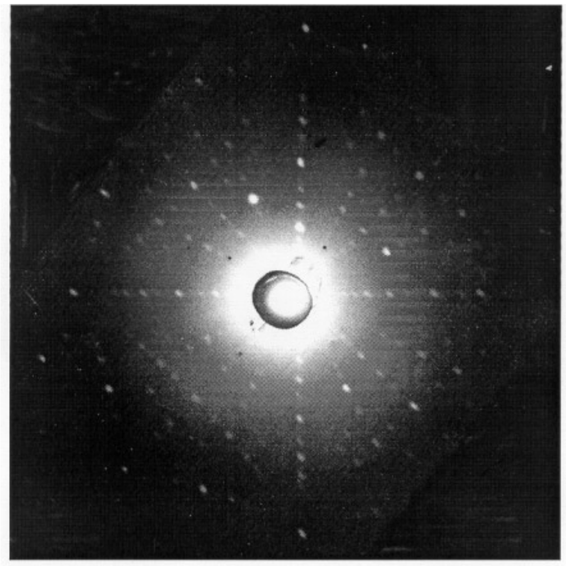


Figure 2. X-ray Laue back reflection photograph of a crystal of $Sm_2Ti_2O_7$, showing the (100) orientation.

is shown in figure 2 and shows that the crystals obtained are of good quality. A few of the crystals have also been examined for their crystal quality using neutrons.

It is possible to grow single crystals of the Ti pyrochlores in oxygen, nitrogen or argon atmospheres instead of in air. A change is seen in the colour of the crystal grown when the growth atmosphere is changed and is an indication of the oxygen nonstoichiometry in the crystals. A study of the differences in properties of the crystals grown in different atmospheres is underway.

The floating zone technique appears to be well suited to the growth of the whole series of rare earth titanate pyrochlores and large crystals can be grown with ease. This is in contrast to the situation that existed earlier where relatively small crystals had been obtained for a few of the pyrochlores by methods involving the use of flux. The floating zone method also has the advantage that crystals can be grown in different gas atmospheres. Detailed investigations, especially of the magnetic frustration at low temperatures using neutron scattering as a probe, can now be carried out with relative ease given the currently available size and quality of crystals.

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