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FAST TRACK COMMUNICATION

High quality single crystals of the SrR_2O_4 family of frustrated magnets

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Abstract
Large high quality single crystals of several compounds of the new family of frustrated magnetic oxides SrR_2O_4 where R = Dy, Er, Ho and their nonmagnetic analogues with R = Lu, Y have been synthesized by the floating zone technique. The magnetic rare earth ions in these compounds are linked to each other through a network of hexagons and triangles reminiscent of the honeycomb lattice. Initial characterization measurements show that geometrical frustration plays an important role in the formation of the magnetic ground states in these systems. The single crystals grown are suitable for more detailed investigations, especially those using neutron scattering techniques.

Recent studies on highly frustrated magnets have shown that they provide a rich source of unforeseen and exciting physics, including novel types of phase transitions, exotic transport phenomena, unusual spin-disordered states with algebraic or power law correlations as well as topological excitations that are classical analogues of magnetic monopoles. In most cases, detailed investigations of the magnetic properties of the compounds with geometric frustration have been possible due to the availability of high quality single crystals. Among the well-known examples are the pyrochlore compounds, where the spin-ice phenomenon in Ising-like $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$ [1], co-operative paramagnetic state in $Tb_2Ti_2O_7$ [2] and unusual H–T phase diagram in Heisenberg-like $Gd_2Ti_2O_7$ [3] have been investigated. Large single crystals [4, 5] have been required for such investigations. The rapid progress made in understanding the behaviour of multiferroic materials with a significant degree of magnetic frustration (such as RMn_2O_5, $Ni_3V_2O_8$, $CuFeO_2$ and $RbFe(MoO_4)_2$) would have been impossible without single crystals. In many other geometrically frustrated magnets (such as the cubic spinel $ZnCr_2O_4$ [6], $Co_3V_2O_8$ with Kagomé staircase structure [7], Ising chain compound $Ca_3Co_2O_6$ [8]) neutron scattering investigations on single crystal samples have provided the most direct information on the ground state and the spectrum of magnetic excitations of these compounds.

Recently, Karunadasa *et al* [9] reported the investigation of the crystal structure and magnetic properties of a series of compounds with the general formula SrR_2O_4, where R = Gd, Dy, Ho, Er, Tm and Yb. It is the arrangement of the R atoms in the structure that makes them interesting candidates for investigation as possible systems that may exhibit magnetic frustration. At room temperature, the crystal structure of the SrR_2O_4 compounds belongs to the space group *Pnam* with the *a* and *b* axes being about 10 and 12 Å long, while the *c* axis is only about 3.4 Å long [9]. The magnetic R atoms are linked together through a network of triangles and hexagons in a honeycomb like arrangement and geometric frustration arises when the exchange interactions are antiferromagnetic. As an indication of the presence of geometric frustration, one should consider the disparity between the reported Curie–Weiss temperatures (−23 K, −17 K and −12 K for $SrDy_2O_4$, $SrHo_2O_4$ and $SrEr_2O_4$ respectively) and the absence of magnetic ordering in any of these compounds at temperatures down to at least 1.5 K [9]. From the literature available on these compounds so far, single crystals do not appear to be available.

In this communication, we describe the growth of single crystals of compounds SrR_2O_4, R = Dy, Er, Ho, Lu and Y, demonstrating for the first time that large high quality single crystals of the SrR_2O_4 family of isostructural compounds can be obtained by the floating zone technique using an optical mirror furnace. The crystals grown are suitable for most physical property characterization measurements and the large volumes needed for neutron scattering measurements may be obtained. The ability to produce crystals of a number

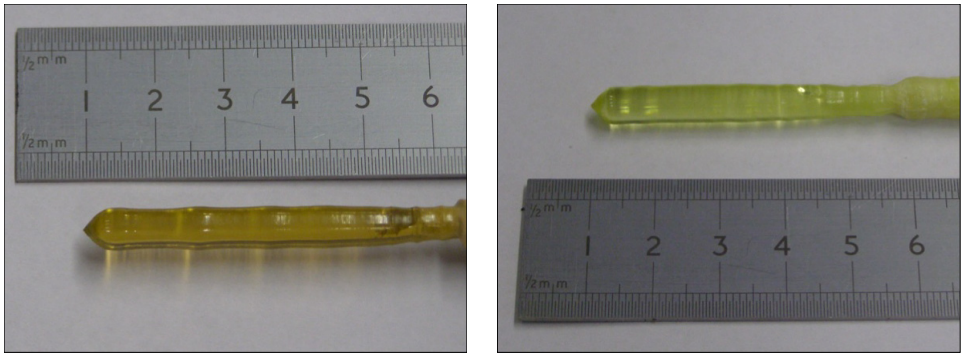

Figure 1. As grown boules of $SrHo_2O_4$ (left panel) and $SrDy_2O_4$ (right panel) single crystals, using growth speeds of 6–8 mm h^{-1}. (This figure is in colour only in the electronic version)

of members of the family is especially important for the systematic study of the magnetic frustration as a function of the rare earth element.

The melting temperatures of this class of compounds is higher than for most typical oxides, being at the limit of or just above the temperature range that is accessible using the halogen lamp optical furnaces (2150 °C). Therefore, for the crystal growth of this family of compounds, an optical furnace equipped with Xe arc lamps was used. Initial characterization of the crystals grown using x-rays and magnetic susceptibility measurements is presented here. More detailed investigations of the magnetic properties of one of the compounds, $SrEr_2O_4$, by magnetization, specific heat and neutron powder diffraction are being published separately [10].

Polycrystalline powders of SrR_2O_4 (R = Dy, Er, Ho, Y, and Lu) were first prepared by conventional solid state synthesis. The starting materials of high purity R_2O_3 (>99.9%) and $SrCO_3$ (99.95%) were mixed together in strictly stoichiometric ratios and reacted in air at 1400 °C for 2–3 days with several intermediate grindings to ensure good homogeneity of the mixture. The resulting powders were then isostatically pressed in the form of rods (7–8 mm diameter and 70–80 mm long) and sintered in air at 1500 °C for 24–48 h. These rods were used for crystal growth in a high temperature optical furnace equipped with four 3 kW Xe arc lamps (CSI Model FZT-12000-X-VI-VP). The feed and seed rods were rotated at 25–30 rpm and the crystal growth was carried out at various growth speeds ranging from 1 to 10 mm h^{-1}. Various atmospheres were tried for the growth of the compounds in this study and the best results were obtained for growths carried out under a flow of high purity argon gas (2 l min^{-1}). For the initial growths, polycrystalline rods were used as seed rods and once satisfactory crystals were obtained, these crystals were used as seeds for subsequent growths. The boules obtained were typically about 6 mm in diameter and about 60–70 mm long. The boules were clear, the colour varying with the rare earth, R. Most of the crystals grown developed facets as they grew and were transparent to light. All the compounds studied here appear to have congruent melting points. The as grown boules of the $SrEr_2O_4$ sometimes tended to develop cracks on cooling even for the slowest growth speeds tried (1 mm h^{-1}), while all the other crystals grown for this study were produced crack free.

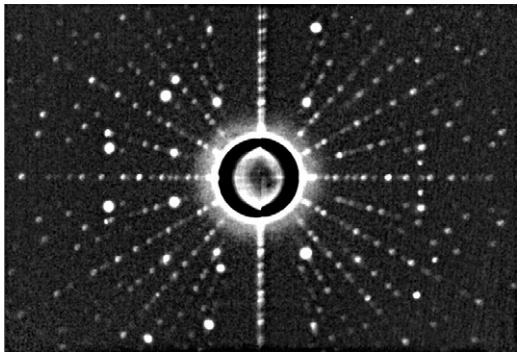

Figure 2. A typical x-ray Laue photograph obtained from a crystal of $SrEr_2O_4$ oriented along the b axis after a 10 min exposure.

Figure 1 shows the as grown boules of two of the crystals of $SrHo_2O_4$ and $SrDy_2O_4$ illustrating the size and volume of the crystals that can be obtained by this technique. The boules were examined prior to cutting by x-ray Laue back reflection. A typical x-ray Laue photograph obtained from a crystal of $SrEr_2O_4$ oriented along the b axis is shown in figure 2. The quality and mosaic of some of the crystals obtained were also examined using neutrons and we have established that their quality is sufficient for single crystal neutron inelastic studies[1]. Small pieces oriented along the three crystallographic axes were cut from the as grown boules for magnetic susceptibility and specific heat measurements. The results of the specific heat measurements are being communicated separately [10].

Magnetic susceptibility was measured using a Quantum Design SQUID magnetometer. Figure 3 shows the magnetic susceptibility of a crystal of $SrEr_2O_4$ measured with the applied magnetic field along the three crystallographic axes, a, b and c. As can be seen, the measured magnetic susceptibility is markedly anisotropic, with the hard axis direction along b. The inset to the figure 3 shows the inverse magnetic susceptibility for $H \parallel a$ over the entire temperature range from 400 to 1.9 K. The data for the inverse susceptibility were fitted to the standard Curie–Weiss formula in the temperature range

[1] Single crystals of $SrEr_2O_4$ examined using the PRISMA spectrometer (ISIS, Rutherford Appleton Laboratory), produced Bragg peaks with mosaic spreads of less than the instrument resolution of 0.5°.

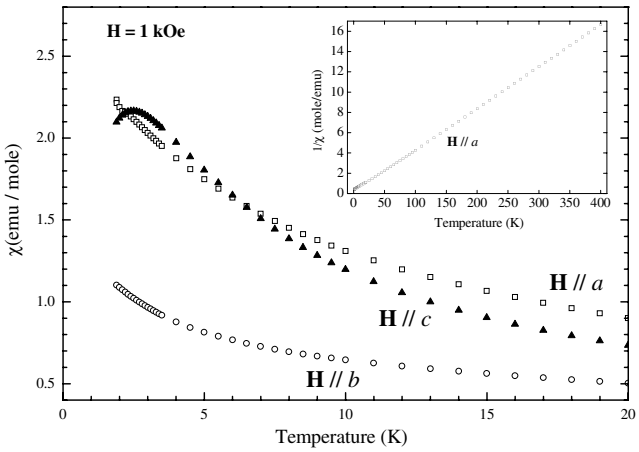

Figure 3. The temperature dependence of the magnetic susceptibility of a crystal of $SrEr_2O_4$ measured with the magnetic field applied along the three different crystallographic directions. The inset to the figure shows the inverse susceptibility as a function of temperature for the same applied field along the *a* axis.

100–400 K, where it is nearly linear with temperature. The estimates obtained for the Weiss temperatures are $\Theta_a \approx -3$ K, $\Theta_b \approx -23$ K and $\Theta_c \approx -11$ K, while Karunadasa *et al* reported $\Theta \approx -12$ K from their susceptibility measurements on polycrystalline powder. The significant difference in Weiss temperatures observed for the different directions of the applied magnetic field suggests a strong influence of the low lying crystal field levels, which is not unusual in rare earth based magnets.

Although the measured susceptibility for $H \parallel c$ in the $SrEr_2O_4$ crystal shows a broad peak at ∼2 K, this does not correspond to the onset of magnetic ordering. Indeed, our measurement of the specific heat down to 300 mK reveals a sharp peak in $C(T)$ at ∼0.75 K, indicating that the system orders magnetically at this temperature [10]. A detailed investigation of the nature of the long range antiferromagnetic ordering and the magnetic structure adopted by $SrEr_2O_4$ below this temperature has been carried out by powder neutron diffraction [10].

From the initial measurements of the magnetic susceptibility and specific heat on just one member of this family, it is clear that there is a need for high quality single crystals to understand the interactions that exist at low temperatures, which either lead to a long range magnetically ordered state or a magnetically frustrated state. The floating zone technique appears to be well suited for producing sufficiently large crystals of this family of compounds for most physical property measurements. It is likely that the single crystals of all the remaining members of the SrR_2O_4 family compounds can be grown using the same technique. There is already sufficient evidence to indicate that these compounds display a rich H–T phase diagram at low temperatures. Detailed investigations of the low temperature phase diagram of these interesting class of compounds are currently in progress using the crystals available.

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