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Crystal growth and magnetic behaviour of pure and doped $SrCu_2(^{11}BO_3)_2$

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Abstract

High quality single crystals of incongruently melting $SrCu_2(BO_3)_2$, both pure and doped with Mg, La and Na have been grown by optical floating zone (OFZ)-image furnace technique using self-flux. The obtained single crystals were characterized by X-ray powder diffraction and by neutron scattering using highly enriched ^{11}B for selected crystals. Magnetic susceptibility measurements from 3 to 300 K, with a magnetic field parallel to the *ab* plane were performed on pure and doped crystals oriented by the Laue method. The measurements show a relatively complex behaviour and confirm the formation of a spin singlet ground state at low temperatures. No evidence of superconductivity is observed.

Keywords: A2. Single-crystal growth; A2. Travelling solvent floating zone technique; B1. Borates; B1. Cuprates; B1. $SrCu_2(BO_3)_2$; B2. Magnetic materials

1. Introduction

Strontium copper borate $SrCu_2(BO_3)_2$ is a highly unusual quantum spin system which has recently attracted attention as the first example of a material realizing the Shastry—Sutherland model of interacting dimers. In this exactly solvable model, antiferromagnetically coupled dimers with intra- and inter-dimer exchange couplings J and J' interact within well separated *ab* planes [1]. Such low-dimensional quantum systems which have a disordered ground state are of great topical interest, due to the diverse and fascinating physics associated with spin liquids. However, while there are many instances of quasi-one-dimensional (1D) spin ladder or chain compounds, there are relatively few good quasi-two-dimensional (2D) experimental examples. The purpose of our work was to obtain large, high-quality crystals with the ^{11}B isotope, suitable for neutron scattering experiments. Due to the incongruent melting of $SrCu_2(BO_3)_2$, this can be achieved only by growing the crystal at a very slow (slower than 0.5 mm/h) rate [2].

To investigate the effects of doping on the physical properties of the material, an attempt was made to introduce Mg, Na, Zn and La into the lattice. It was expected that substituting Cu^{2+} site with Zn^{2+} or Mg^{2+} would destroy the planar order, [3] whereas Na^{1+} or La^{3+} substituting for Sr^{2+} would donate electrons/holes to the 2D sheets [4].

Undoped single crystals of $SrCu_2(BO_3)_2$ have previously been grown by using the travelling solvent floating zone (TSFZ) method by Kageyama [5]. In this work, $LiBO_2$ was used as a flux (solvent) and the growth rate of 0.5 mm/h was employed. The properties of these crystals are discussed by Miyahara et al. [6]. $SrCu_2(BO_3)_2$ crystals up to 7 mm × 7 mm × 2 mm in size have also been grown by Maltsev et al. [7] by the slow cooling/evaporation method from $Na_2B_4O_7$ flux, using Pt crucibles.

2. Experimental procedure

2.1. Ceramics preparation

Powders of $SrCO_3$ (Puratronic, 99.9985), La_2O_3 (CERAC, 99.99), $MgCO_3$ (Puratronic, 99.996), Na_2CO_3 (BDH

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99.99), B_2O_3 (CERAC, 99.9) and CuO (CERAC, 99.999) were used as starting materials. Enriched $^{11}B_2O_3$ powder was purchased from Eagle Picher Boron (99.62 isotopic purity). Before weighing, $SrCO_3$, $MgCO_3$ and CuO were annealed at 400 °C; La_2O_3 was annealed at 1000 °C and weighed immediately. In the case of B_2O_3 and $^{11}B_2O_3$, the corrections for weight loss at 400 °C were determined.

The powders were mixed in stoichiometric proportions and pre-reacted at 780 °C according to the reaction

$$SrCO_3+2CuO + B_2O_3 \rightarrow SrCu_2(BO_3)_2+CO_2.$$

A gray, polycrystalline powder of $SrCu_2(BO_3)_2$ was obtained and crushed in a ballmill for 24–48 h in a polyethylene container, using ZrO_2 balls. Subsequently, the material was loaded into a rubber tube and pressed hydrostatically at 65 MPa to produce rods of about 7 mm in diameter and 100 mm in length. These rods were sintered at 780 °C and then re-ground and sintered at 810 °C in air for 24 h. The rod color changed from gray to blue after the second sintering. The material was then re-ground, pressed and annealed again at 840 °C in flowing O_2 for 70 h. After this annealing the blue color intensified substantially. The density of the as-obtained rod was 2.64 g/cm^3, about 64% of the crystallographic density ($d_x = 4.103$ g/cm^3 [8]). The rods were densified before the final growth by premelting in O_2 using the floating zone apparatus ($d_{premelt} = 3.05$ g/cm^3). The rods obtained were about 10 cm long, dark blue, matte, with two well-defined facets parallel to the growth direction. A cross-section at the end of the growth revealed many grains. Fig. 1 shows La doped rods premelted with the speed of 20–25 mm/h. According to our preliminary differential thermal analysis experiment, the $SrCu_2(BO_3)_2$ material melts incongruently at 970 (±5) °C.

2.2. Crystal growth of pure $SrCu_2(BO_3)_2$

Single crystals of $SrCu_2(BO_3)_2$ were grown using an optical floating zone technique in a Crystal Systems Inc. image furnace with 4 halogen lamps of 300 W each. All the growth experiments were performed in 2 atm of O_2. Platinum wire was used to attach both rods to their holders. In preliminary experiments, a premelted ceramic rod was used as a seed. The solidified tip of the rod from the premelt run (with steady state composition) was used as the self-flux for the crystal growth. During crystal growth both seed and feed rods rotated in opposite directions (20–30 rpm). A photograph of the zone is presented on Fig. 2. After 4 cm of growth the experiment was terminated and we found large crystalline grains at the end of growth rod. This rod was then used as a seed for the next experiment.

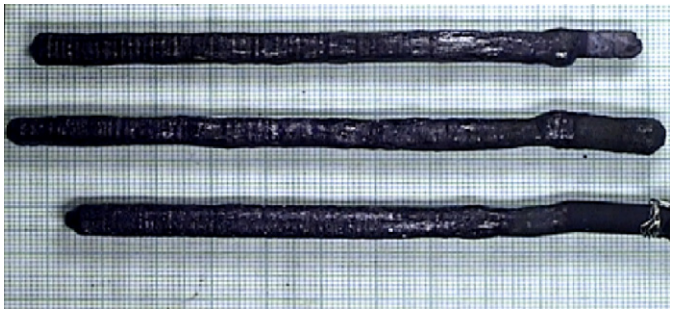

Fig. 1. $La_{0.04}Sr_{0.96}Cu_2(BO_3)_2$ rods premelted with the speed of 25 mm/h.

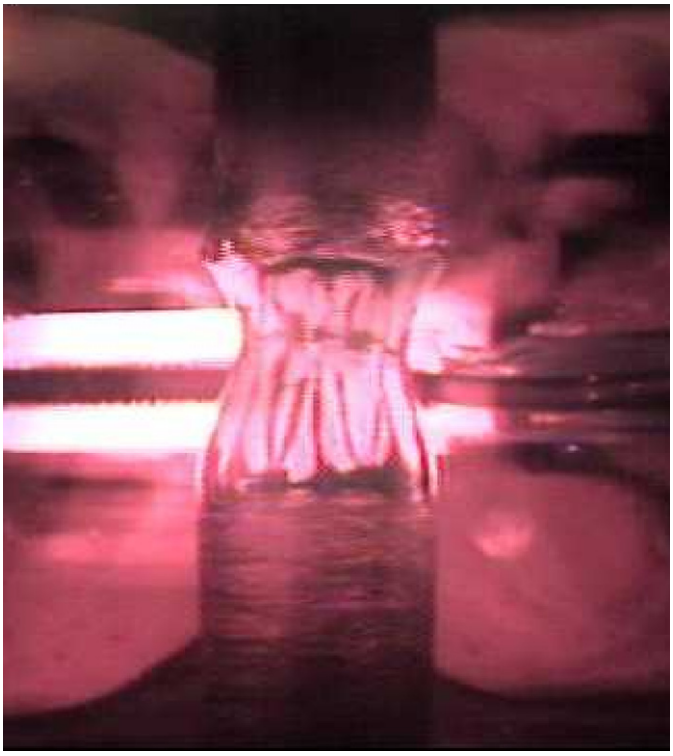

Fig. 2. The shape of the zone in the growth of $La_{0.04}Sr_{0.96}Cu_2(BO_3)_2$ crystal from premelted rod with the speed of 0.25 mm/h in O_2.

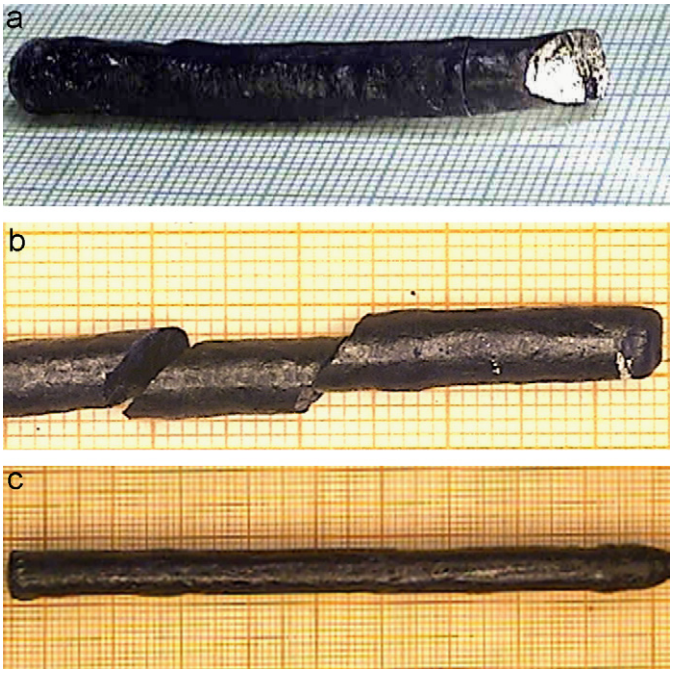

Fig. 3. Single crystal of $SrCu_2(BO_3)_2$.