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Crystal growth and characterization of the non-centrosymmetric antiferromagnet $Ba_2CuGe_2O_7$

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ABSTRACT

It is well known that non-centrosymmetric tetragonal antiferromagnets can host a number of interesting properties, including multiferroicity as well as magnetic skyrmions and $Ba_2CuGe_2O_7$ is one notable example. The study of all these complex phenomena requires the availability of good crystals. We have carried out the single crystal growth of the helimagnet $Ba_2CuGe_2O_7$ by the floating zone technique, using different gas atmospheres and pressures and report the optimal growth conditions allowing the synthesis of large crystals. X-ray Laue back reflection has been used to determine the orientations of the as-grown crystals. The morphology and chemical composition of the crystals have been investigated by scanning electron microscopy (SEM) with wavelength dispersive spectrometry (WDS). By using powder X-ray diffraction and energy dispersive spectroscopy (EDS) maps, the composition of the starting polycrystalline rods was checked. Powder X-ray diffraction has been also used to check the composition of the grown single crystals. Furthermore, the excellent quality of the $Ba_2CuGe_2O_7$ crystals was confirmed by rocking curve measurements, giving a FWHM of $\sim 0.012^{\circ}$. The crystal growth parameters reported in this work allow the synthesis of high quality single crystals suitable for detailed investigations of the complex magnetic phase diagram of this non-centrosymmetric compound.

1. Introduction

In recent years, the understanding of the multiferroic properties, i.e. of the simultaneous presence of two or more coexisting ferroic orders, has been the topic of increasing interest [1,2]. Indeed, the coexistence in multiferroics of spontaneous magnetization M and polarization P that may respond to relatively weak external electric and magnetic fields respectively, implies potential applications in spintronics devices [3–6]. As a matter of fact, the attention to multiferroics has been mainly driven by the large magnetoelectric (ME) coupling shown by some distorted perovskites of transition metal (TM) oxides displaying both ferroelectric and magnetic properties [7–9]. Furthermore, very recently a so-called spin-dependent hybridization mechanism, where spin-orbit coupling (SOC) induces anisotropic charge-transfer effects between the TM cation and the surrounding oxygens, has been devised for this class of oxides, giving rise to local electric dipoles [10–14]. A necessary ingredient for this mechanism to be realized is the local arrangement of the TM cation with respect to the ligand oxygen, which needs to lack inversion symmetry, e.g. for tetrahedral coordination. The materials with the non-centrosymmetric crystal structure $Ba_2TMGe_2O_7$, consisting of Ge_2O_7 dimers linked by TMO_4 tetrahedra, represent an ideal playground where the properties of TM ions with tetrahedral coordination could be explored in detail [11]. Among this class of compounds, the study of the helimagnet $Ba_2CuGe_2O_7$ is of great interest [15]. This interest has received a further boost due to the theoretical prediction that it could host a lattice of magnetic skyrmions [16], i.e. topologically protected particle-like magnetic "bubbles" with a vortex-like spin texture that could be used for data-storage applications. Nevertheless, up to now no detailed study of the magnetic domains and their microscopic relation to the ferroelectric properties has been performed. For the above reasons, we have attempted to grow large and pure single crystals of $Ba_2CuGe_2O_7$ which can be used to determine its magnetic domain structure.

In this study, we demonstrate the successful growth of high quality $Ba_2CuGe_2O_7$ single crystals using the floating zone (FZ) technique, in different gas atmospheres and pressures. The high crystallinity of the as-grown crystals has been confirmed by high resolution X-ray measurements.

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2. Experimental procedures

2.1. Powder synthesis

The starting materials for the preparation of feed and seed rods for growing $Ba_2CuGe_2O_7$ crystals were $BaCO_3$ (Sigma Aldrich 99.999%); CuO (MV Laboratories 99.9999%) and GeO_2 (Alfa Aesar, 99.9999%). The $Ba_2CuGe_2O_7$ polycrystalline rods were prepared by conventional solid state reactions at high temperature. We adopted two different methods, called "A" and "B" in the following, for making single phase polycrystalline rods. In both methods, before the reactions, $BaCO_3$ was pre-annealed at 500 °C for 1 h, and then mixed with the other starting materials, in stoichiometric proportions and heated. In method "A" three thermal treatments at 850 °C for 24 h, 900 °C for 24 h and 950 °C for 15 h with intermediate grindings were performed. After cooling down, the synthesized powder was thoroughly reground and the powder was isostatically pressed for about 10 min in water to a pressure of approximately 50 MPa. The resulting cylindrical rods were sintered in a furnace, in a vertical position, at 980 °C in air for 15 h. In method "B" both the $BaCO_3$, and the GeO_2 were pre-annealed, the latter at 800 °C [17]. The pre-annealing of both $BaCO_3$ and GeO_2 produced dried powders guaranteeing the mixing of the powders in the desired stoichiometry. Moreover, X-ray analysis on GeO_2 powder performed before and after the 800 °C thermal treatment showed a partial transition from α-quartz to the rutile-type structure. It is well known that GeO_2 exhibits several polymorphs [18–21] that mainly differ in their chemical properties, especially solubility and densities. Hence the reaction of GeO_2 in our system, depending on the phase stability and microstructure, is favoured by the thermal treatment. Concerning the method "B", after the pre-annealing, mixtures of starting materials in stoichiometric proportions were heated at 880 °C for 15 h, 950 °C for 20 h and 980 °C for 60 h with intermediate grinding. Finally, the rods were prepared as in the method "A". In both methods, the resulting sintered rods were typically 6–7 mm in diameter and 60–90 mm in length and their densities was determined to be about 85% of the theoretical density of $Ba_2CuGe_2O_7$. Single phase identification was performed by X-ray powder diffraction (XRD).

2.2. Crystal growth

For growing single crystals in this study, we employed the floating zone method using two types of optical image furnaces with elliptical mirrors. One has double-elliptical mirrors (NEC Machinery, model SC1-MDH11020 at CNR-SPIN Salerno) with two 2.0 kW halogen lamps. The other has four elliptical mirrors (Crystal System, model F-ZT-10000-H-IV-VPS at the University of Warwick) with four 500 W halogen lamps. After several attempts of crystal growth, varying the growth conditions, including the speeds of the feed rod and the seed crystal, the counter-rotation speeds and the gas atmosphere, large single crystals with high crystalline quality were obtained. The entire set of growth parameters attempted are summarized in Table 1.

We can see that the rods from method "A" give mixed phase (batches No. 1 and 2) or small crystals (batches No. 3–6) for low growth speed. Improving the quality of the starting polycrystalline rods with method "B", as discussed later, we get bigger and purer crystals (batches No. 8–13). Moreover, from the results summarized in Table 1 we can deduce that the rotation speed, responsible for mixing of material and for the shape of the crystallization front, and the furnace type, strictly related to the temperature distribution within the molten zone [22], greatly influence the size and the colour of the crystals. In fact, comparing the results for batches No. 7 and No. 8 we can see that for the same growth conditions only increasing the rotation speed we change the crystal size. From a comparison of batch No. 8, grown using a two mirror furnace with rotation speeds of 20 rpm, and batch No. 13, grown using a four mirror furnace with a rotation speeds of 30 rpm, we can observe that they show a change in the colour of crystal and this may be related to a combination of two factors: a diverse temperature gradient within the molten zone, related to the different crystal growth furnace used, and to a change of the shape of the crystallization front, due to a change in the rotation speeds. The best results were obtained for a growth rate of 0.5 mm/h, a rotation speed for both rods of 15–30 rpm and an atmosphere of pure O_2 or dried air at a pressure of 5.5 or 3 bar, respectively. It is worth mentioning that the best crystals were obtained starting from feed rods obtained by method "B". This method, as further discussed later in Section 3, assured polycrystalline rods with the right $Ba_2CuGe_2O_7$ phase. This is an important factor in order to achieve a stable liquid zone producing large crystals [22].

2.3. Characterization

The phase composition of the starting polycrystalline rods and of the grown crystals was checked by powder X-ray diffraction using a Bruker D5005 X-ray powder diffractometer employing Cu $K\alpha$ radiation ($\lambda = 1.54$ Å). Rietveld refinement using the FULLPROF code [23] was performed on the θ–2θ scans from 10° to 110° in order to check the phase purity.

Table 1
Summary of crystal quality with varying growth conditions.

Batch No.	Feed rod preparation method	Growth speed (mm/h)	Rotation of feed/seed rods (rpm)	Atmosphere	*P* (bar)	Characteristic of crystal boule
1	**A**	**5**	**40/40**	**Dried Air**	**1**	**Polycrystalline mixed phases**
2	**A**	**5**	**33/33**	**O_2**	**1**	**Polycrystalline mixed phases**
3	**A**	**0.5**	**30/30**	**O_2**	**1**	**Small transparent yellowish crystals**
4	**A**	**1.5**	**10/10**	**Dried Air**	**5.5**	**Small transparent yellowish crystals**
5	**A**	**0.5**	**20/20**	**Dried Air**	**5.5**	**Small transparent yellowish crystals**
6*	**A**	**0.5**	**30/30**	**O_2**	**3**	**Small transparent yellowish crystals**
7	**B**	**0.5**	**10/10**	**O_2**	**3**	**Small dark yellow crystals**
8	**B**	**0.5**	**20/20**	**O_2**	**3**	**Large dark yellow crystals**
9	**B**	**0.5**	**15/15**	**Dried Air**	**5.5**	**Large transparent yellowish crystals**
10	**B**	**0.5**	**25/25**	**Dried Air**	**5.5**	**Large transparent yellowish crystals**
11	**B**	**0.5**	**25/25**	**Dried Air**	**5.5**	**Large transparent yellowish crystals**
12	**B**	**0.5**	**25/25**	**Dried Air**	**5.5**	**Large transparent yellowish crystals**
13*	**B**	**0.5**	**30/30**	**O_2**	**3**	**Large transparent yellowish crystals**

The crystals labelled by the superscript (∗) were grown using a four mirror furnace, while all the other growths were performed employing a two mirror furnace. *P* is total pressure in the quartz tube.