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Growth of single-crystals of rare-earth zirconate pyrochlores, $Ln_2Zr_2O_7$ (with Ln=La, Nd, Sm, and Gd) by the floating zone technique

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ABSTRACT

The geometrical frustration occurring in the crystal lattice of pyrochlore oxides of the type $A_2B_2O_7$ (where A=Rare Earth, B=Mo, Sn, Ti, Zr) leads to exotic magnetic properties of these materials. The present study focuses on a new class of frustrated magnets, the lanthanide zirconates. Large, high quality single-crystals of the rare-earth zirconium oxides, $Ln_2Zr_2O_7$ (where Ln=La, Nd, Sm, and Gd), have been grown by the floating zone technique, using a high power xenon arc lamp furnace. The crystals have been characterized and tested for their quality using X-ray diffraction techniques.

1. Introduction

Pyrochlore oxides, $A_2^{3+}B_2^{4+}O_7$ (where A= trivalent rare-earth metal, B= tetravalent transition metal), have been thoroughly investigated over the past two decades, both theoretically and experimentally [1]. The stability field diagram established by Subramanian et al. shows a wide array of elements (both for the A and B sites) form as the $A_2^{3+}B_2^{4+}O_7$ pyrochlore phase [2]. The geometrically frustrated network of corner sharing tetrahedra of the metal ion sites (both A and B sites) and the nature of these ions leads to a large variety of unusual magnetic behaviors [1].

Considerable progress has been made in the field of frustrated magnetism due to breakthroughs in the preparation of large, high quality single-crystals of various pyrochlores. It was first shown that large single crystals of the rare-earth titanate pyrochlores $A_2^{3+}Ti_2O_7$ (where A= Pr, Nd, Sm, Tb, Dy, Ho, Er, Y) could be produced by the floating zone technique [3,4]. Subsequently, crystals of the entire series of rare-earth titanates $A_2^{3+}Ti_2O_7$ (A = Pr → Lu) [5–8] were grown, their structural and magnetic properties investigated in detail, and their magnetic ground states elucidated [6,7,9–11]. Recently, crystals of the molybdate family, $A_2Mo_2O_7$ (where A=Nd, Sm, Gd, Tb, Dy) [12,13], have also been grown using the floating zone technique and their properties studied [13–17].

The research community has recently shown an increased interest in the lanthanide zirconates, $Ln_2Zr_2O_7$, both due to their potential use in the immobilization of radioactive waste [18] and in thermal barrier coatings [19], and in the quest for materials which exhibit quantum spin liquid or quantum spin ice behavior [20,21]. Lanthanide zirconium oxides crystallize in the cubic structure at room temperature and at ambient pressures. Nevertheless, depending on the ionic radius ratio of the two metallic ions, RR = $(r_{Ln^{3+}}/r_{Zr^{4+}})$, their structure can be stabilized with one of two different space groups, either $Fd\bar{3}m$ (No. 227), which corresponds to the pyrochlore structure (large lanthanide elements), or $Fm\bar{3}m$ (No. 225), belonging to the defect-fluorite structure (for small lanthanide elements) [2].

Lanthanide zirconates, $Ln_2Zr_2O_7$ (with Ln = Tb → Lu), with the ionic radius ratio, RR, ranging from 1.44 to 1.35, crystallize in a defect-fluorite structure [2]. Compounds $Ln_2Zr_2O_7$ (where Ln = La → Gd), with the ionic radius ratio, RR, ranging from 1.61 to 1.46, adopt the cubic pyrochlore structure [2]. Their crystallographic structure contains two different cation sites and two distinct anion sites; the large trivalent rare-earth Ln^{3+} ions occupy the eight-fold oxygen coordinated A sites, while the six-fold coordination of the B sites is filled by the smaller tetravalent zirconium ions Zr^{4+} [2].

At high temperature ($T > 1500$ °C), lanthanide zirconates $Ln_2Zr_2O_7$ (where Ln = Nd → Gd) undergo an order–disorder transition from a pyrochlore to a defect-fluorite structure. The transition temperature depends on the nature of the rare-earth ion [2,22–24]. Therefore,

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lanthanum zirconate exists only in the pyrochlore form, whereas for neodymium, samarium, and the gadolinium zirconates, a transition from a pyrochlore to a defect-fluorite structure occurs at 2300, 2000, and 1530 °C respectively [22]. Furthermore, recent studies have shown that the lanthanide zirconates with a pyrochlore structure are not stable at high pressure and that they undergo a pressure induced structural transformation leading to either a monoclinic phase (space group $P2_1/c$) [25,26], or a defect cotunnite-type structure (space group *Pnma*) [27].

Due to the high melting point of the lanthanide zirconate pyrochlores [28], it has proven difficult to obtain crystals of these materials and until recently the structural and magnetic properties of this new class of pyrochlore oxides have only been studied using powder samples [22,23,29–35].

Roth showed in a previous study of the phase diagram of Ln_2O_3–ZrO_2 (where Ln=La and Nd) [28] that the pyrochlore type oxides melt congruently above 2000 °C. Single-crystals of the zirconates pyrochlore family can therefore be grown by the floating zone technique but due to the high melting point of these oxides, the crystal growth using optical furnaces can only be carried out with a high power xenon arc lamp furnace.

In this paper, we report the growth, for the first time, of single-crystals of the lanthanide zirconates pyrochlores, $Ln_2Zr_2O_7$ (where Ln=La, Nd, Sm, and Gd). Recent studies [20,36–38] have shown the feasibility of the floating zone technique for preparing single-crystals of one member of the zirconate family, $Pr_2Zr_2O_7$. The present study demonstrates that large, high quality crystals of a number of pyrochlore lanthanide zirconates may be grown using this technique. This is especially important for the study of the properties of this new class of geometrically frustrated magnets and particularly for solving the nature of their magnetic ground states.

2. Experimental details

The $Ln_2Zr_2O_7$ (where Ln=La, Nd, Sm, and Gd) pyrochlore oxides were first synthesized in polycrystalline form by reacting powders of the starting oxides, Ln_2O_3 (99.9%) and ZrO_2 (99%). Stoichiometric amounts of the powders were ground together and calcined in air for several days at temperatures in the range 1300–1450 °C with intermediate grindings. The resulting material was then isostatically pressed into rods (typically 6–8 mm diameter and 70–80 mm long) and sintered at 1450–1600 °C in air for several days. X-ray diffraction patterns of powdered pieces of the rods were recorded on a Panalytical X-Ray diffractometer with a Cu $K\alpha_1$ anode (λ=1.5406 Å). The diffraction patterns were collected at room temperature and over an angular range of 10–110° 2θ with a step size of 0.013° in 2θ and a total scanning time of 16 h. The analysis of the X-ray patterns was performed using the Fullprof software suite [39].

Crystals of the lanthanide zirconate, $Ln_2Zr_2O_7$, were grown in air or in oxygen atmospheres. The growths were carried out in a four-mirror xenon arc lamp optical image furnace (CSI FZ-T-12000-X_VI-VP, Crystal Systems Incorporated, Japan), at growth speeds in the range 5–15 mm/h. Initially, polycrystalline rods were used as seeds and once good quality crystals were obtained, a crystal seed was used for subsequent growths. The two rods (feed and seed) were counter-rotated at a rate of 20–30 rpm.

To analyze the microstructure and to investigate the crystal perfection of the floating zone-grown crystals, pieces of the $Nd_2Zr_2O_7$ boules were cut along the growth direction, polished and studied using polarized light microscopy.

The quality of the as-grown crystals was checked using a Laue X-ray imaging system with a Photonic-Science Laue camera system.

Small quantities of each crystal were ground into powder and powder X-ray diffraction measurements were performed to determine the phase purity and to establish the crystallographic structure of the $Ln_2Zr_2O_7$ crystals. It is important to determine whether the lanthanide zirconates boules have crystallized in either the pyrochlore or the defect-fluorite phase. Room temperature diffractograms were collected on a Bruker D5005 X-ray diffractometer using Cu $K\alpha_1$ and $K\alpha_2$ radiation ($\lambda_{K\alpha1}=1.5406$ Å and $\lambda_{K\alpha2}=1.5444$ Å), between 10° and 110° 2θ, with a step size of 0.016° in 2θ, and a total scanning time of 24 h. The patterns were then analyzed using the Fullprof software suite [39].

3. Results and discussion

Lanthanide zirconate $Ln_2Zr_2O_7$ (where Ln=La, Nd, Sm, and Gd) crystals were grown by the floating zone method, using different growth conditions. A summary of the conditions used is given in Table 1. All the Zr-based pyrochlores grown appear to melt congruently and little or no evaporation was observed for any of the growths. Crystals of $Ln_2Zr_2O_7$ were successfully grown using various growth rates, however larger monocrystalline samples were isolated from the crystal boules prepared using higher growth speeds. In the following sections, we describe the crystal growth of each lanthanide zirconate.

3.1. $La_2Zr_2O_7$

$La_2Zr_2O_7$ feed rods were sintered at 1550 °C in air for 2 days. Analysis of room temperature powder X-ray diffraction patterns collected on powdered sections of the polycrystalline rods provided a good fit

Table 1
Summary of the conditions used for the growth of $Ln_2Zr_2O_7$ (where Ln= La, Nd, Sm, and Gd) crystals. All the boules grown were transparent to light.

$Ln_2Zr_2O_7$	Growth rate (mm/h)	Atmosphere	Pressure	Rod rotation rate (rpm)	Color of crystal boule
$La_2Zr_2O_7$	12.5–15	Air	Ambient	20–30	Colorless
$Nd_2Zr_2O_7$	10–15	Air	Ambient	20–30	Dark-purple
$Sm_2Zr_2O_7$	5–15	O_2	4 bars	20–30	Light-orange
$Gd_2Zr_2O_7$	10–15	Air	Ambient	20–30	Light-yellow

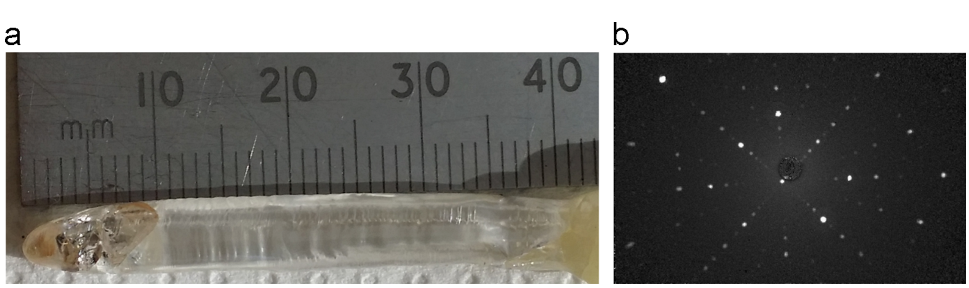

Fig. 1. (a) Boule of $La_2Zr_2O_7$ prepared by the floating zone method in air at a growth rate of 15 mm/h. (b) X-ray Laue back reflection photograph taken for one of the facets of a $La_2Zr_2O_7$ crystal.