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Synthesis and characterization of single crystalline $Gd_5(Si_xGe_{1-x})_4$ by the Bridgman method

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Abstract

Single crystals of $Gd_5(Si_xGe_{1-x})_4$ have been prepared by the Bridgman method using tungsten crucibles. The tungsten crucible was found to be chemically inert with respect to Gd, Si, Ge but did have limited solubility in liquid $Gd_5Si_2Ge_2$, resulting in the precipitation of pure tungsten throughout the bulk crystal. Overall, the bulk crystal solidified in the monoclinic phase and a slight increase in Si content and decrease in Ge content at the growth proceeded was found. This increase in Si:Ge ratio resulted in a slight increase in lattice parameter of the monoclinic phase and an increase in the magnetostructural transformation temperature of $\Delta T = 10$ K. AC susceptibility measurements indicated a small fraction of orthorhombic phase was present throughout the ingot which accounts for the decrease in MCE values along the length of the ingot.

Keywords: $Gd_5Si_2Ge_2$; Magnetocaloric; Magnetically ordered materials; Crystal growth; Magnetic measurements

1. Introduction

In recent years, the family of compounds $Gd_5(Si_xGe_{1-x})_4$ has received a great deal of attention due to their unique magnetic properties including giant magnetocaloric effect [1,2], colossal magnetostriction [3,4] and giant magnetoresistance [5,6]. These extraordinary responses result from a first-order magnetostructural transformation from a paramagnetic monoclinic high temperature phase into a ferromagnetic orthorhombic phase [6–9]. The magnetic and structural aspects of the transformation have been investigated extensively using polycrystalline materials and the low temperature phase diagram is well established [7–20]. Structural determination of the monoclinic and orthorhombic polymorphs have been carried out by single crystal X-ray diffraction, however large single crystals have not been readily available to investigate the anisotropic material properties of these compounds.

In this paper we describe our efforts to synthesize single crystals of $Gd_5(Si_xGe_{1-x})_4$ by the Bridgman method using refractory metal crucibles. Crystal growth is hampered by the high melting point of the compounds (>2073 K) and the reactivity of both the rare-earth metal and silicon at these temperatures. Successful bulk single crystal growth from the melt also relies on knowledge of the phase equilibria, however, the phase diagram of $Gd_5(Si_xGe_{1-x})_4$ at high temperatures is not well known. It is believed that the monoclinic phase is stable up to its melting point. The actual melting behavior of the monoclinic phase, however, is not known but can be assumed to be peritectic in character by comparison to the binary Gd_5Si_4 and Gd_5Ge_4 compounds where either the Gd_5Ge_3 phase is the primary solidification product for Ge-rich compositions or GdSi for Si-rich compositions. Slow solidification through the incongruent melting point will likely yield second phase [21] prior to or concurrent with the monoclinic phase and in the least, lead to compositional variations along the length of the crystal [22]. Since the magnetostructural transformation is highly sensitive to composition (Si–Ge ratio), fluctuations in composition during growth of the crystal will likely lead to structural modifications and variations in magnetic properties. At intermediate temperatures (<1073 K), the monoclinic phase can decompose irreversibly to the orthorhombic variant depending on the heating/cooling rate [23–25]. The monoclinic phase can be retained to room

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temperature by isothermal annealing at temperatures above 1573 °C followed by fast cooling through the intermediate temperature range. With these aspects of the phase equilibria in mind, the as-grown crystals have been characterized using microstructural and compositional analyses along the direction of growth. In addition the crucible–crystal interface was examined for reaction of $Gd_5(Si_xGe_{1-x})_4$ with the crucible. The effect of crucible interactions and compositional segregation on the structure, magnetic properties and magnetostructural transformation are described here.

2. Experimental procedure

Appropriate quantities of gadolinium (99.9 at.% purity), silicon (99.9999%) and germanium (99.999%) for a nominal composition of $Gd_5Si_2Ge_2$ were cleaned and arc melted several times under an argon atmosphere. The Gd was prepared by the Materials Preparation Center at the Ames Laboratory, and contained the following major impurities in ppm-at.%: O ∼ 440, C ∼ 200, H ∼ 160, N ∼ 90, Fe ∼ 40, and F ∼ 30. The buttons were then re-melted to ensure compositional homogeneity throughout the ingot and the alloy drop cast into a copper chill cast mold. Conical tipped tungsten crucible, fabricated by chemical vapor deposition, was used for crystal growth. The as-cast ingot was electron beam welded under vacuum into the crucible for crystal growth. The ingot was heated in a tungsten-mesh resistance furnace under a pressure of 8.8×10^{-5} Pa up to 1273 K and held at this temperature for 1 h to degas the crucible and furnace chamber. The chamber was then backfilled to a pressure of 3.4×10^4 Pa with high purity argon. The ingot was then heated to 2273 K and held at this temperature for 1 h to allow thorough mixing before withdrawing the sample from the heat zone at a rate of 4 mm/h.

The as-grown crystal was sectioned by electro-discharge machining, both longitudinally and transverse to the growth direction, to examine the microstructural development and compositional homogeneity during solidification using scanning electron microscopy with energy dispersive analysis. Samples were taken from the bottom of the ingot (first to solidify) and its top (end of crystal growth) to characterize the changes in structure, composition, magnetic properties and the magnetostructural transition which occurred during crystal growth. Structural characterization was done using powder X-ray diffraction of crushed single crystalline $Gd_5Si_2Ge_2$ and magnetization measurements were carried out in a LakeShore magnetometer susceptometer (model 7225).

3. Results and discussion

3.1. Macroscopic features

Fig. 1 shows a longitudinal section of a typical, as-grown ingot of $Gd_5Si_2Ge_2$. In most cases, the ingot is comprised of large single crystalline grains that are elongated in the solidification direction. Also apparent is the severe cracking of the compound believed to result from a combination of the extreme brittleness of this compound, strong mechanical bond between $Gd_5Si_2Ge_2$ and the crucible and differential thermal contraction between the $Gd_5Si_2Ge_2$ and the tungsten crucible. Orientational analysis by back reflection Laue method of the fracture surfaces did not reveal a preferential cleavage plane. Unfortunately this fragmentation of the crystals within the ingot limits the ability to harvest single crystal specimens of large dimensions.

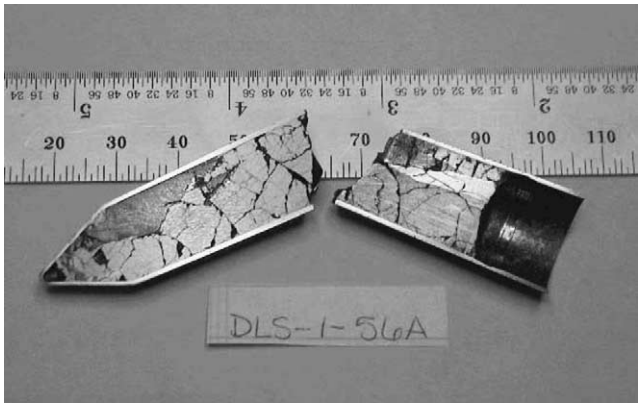

Fig. 1. Longitudinal section of a typical as-grown $Gd_5Si_2Ge_2$ ingot. The ingot is comprised of 3–4 single crystals and is severely cracked along the entire length.

3.2. Crucible/$Gd_5Si_2Ge_2$ interactions

Fig. 2 contains the micrographs of the crucible wall/$Gd_5Si_2Ge_2$ interface and crucible/melt interface. In general, no chemical interactions (such as formation of tungsten silicide or germanide) were observed at the crucible wall. The crucible wall does show a degree of roughening that accounts for the strong mechanical bond between the alloy and the crucible. Occasionally needles or plates of pure W (determined by energy dispersive spectroscopy) were found to protrude out from the wall a few millimeters into the ingot. In addition to the tungsten re-precipitating on the crucible wall, pure tungsten dendrites, Fig. 3, were found within the bulk of the alloy indicating that liquid $Gd_5Si_2Ge_2$ has a small but finite solubility for tungsten. These dendrites were aligned with the growth axis of the ingot and likely solidified directly from the liquid ahead of the solidifying $Gd_5Si_2Ge_2$ solid. The source of this tungsten can be found at the crucible/melt interface shown in Fig. 2b. $Gd_5Si_2Ge_2$ appears to wet the tungsten crucible as evidenced by the slightly concave meniscus at the ingot/crucible interface. Just above the melt line, a reduction of approximately 25% of the crucible wall thickness is observed and likely results from either convective fluid flow on the surface of the melt or from refluxing vapor in the open volume above the melt.