Effects of mechanical grinding and low temperature annealing on crystal structure of Er$_5$Si$_4$

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ABSTRACT

The effect of mechanical grinding and subsequent low temperature annealing on the orthorhombic to monoclinic structural transition in the Er$_5$Si$_4$ compound was studied by X-ray powder diffraction using both a conventional laboratory Cu Kα_1 radiation and a high-energy synchrotron source. A reversible phase transition from the orthorhombic to monoclinic structure occurs as a result of mechanical grinding. Low temperature annealing reverses the transformation and converts the formed monoclinic phase back to the orthorhombic, evidently by relieving residual stress introduced during the grinding.

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1. Introduction

The rare-earth-based intermetallic compounds R$_5$(Si$_x$Ge$_{1-x}$)$_4$, where R are the lanthanides, is a family of magnetocaloric materials first studied by Smith et al. in 1966 [1]. After the giant magnetocaloric effect was discovered in Gd$_5$Si$_2$Ge$_2$ in 1997 [2], this family of materials has captured the attention of researchers all over the world and has led to extensive studies of the magnetic properties and the microstructures of these intermetallic compounds. Smith et al. believed that both the R$_5$Si$_4$ silicides and R$_5$Ge$_4$ germanides crystallize with the Sm$_5$Ge$_4$ type orthorhombic structure [3]. However, Holtzberg et al. [4] noted that the crystal structures of R$_5$Si$_4$ and R$_5$Ge$_4$ were in fact different.

The R$_5$(Si$_x$Ge$_{1-x}$)$_4$ compounds are layered structures [3,5] consisting of essentially equivalent sub-nanometer thick two-dimensional atomic slabs. The absence or presence of Si(Ge)–Si(Ge) covalent-like bonds between these slabs determine the crystal structure and the type of magnetic ordering of the compounds. Three main crystal structures in the R$_5$Si$_4$ and R$_5$Ge$_4$ alloys are: (1) the O(II) Sm$_5$Ge$_4$-type orthorhombic structure (Pnma) with weak inter-slab Si(Ge)–Si(Ge) bonds; (2) the M Gd$_5$Si$_2$Ge$_2$-type monoclinic structure (P112$_1$/a) with alternating strongly and weakly interacting slabs since one half of the inter-slab bonds are present and the other half are broken; and (3) the O(I) Gd$_5$Si$_4$-type orthorhombic structure (Pnma) with all the inter-slab Si(Ge)–Si(Ge) bonds being short and relatively strong.

The phase transformations between these structures can be induced by a number of external triggers such as temperature, applied magnetic field, pressure and chemical composition, which in turn leads to a change in magnetic ordering of the R$_5$(Si$_x$Ge$_{1-x}$)$_4$ intermetallic compounds [5–13]. Many of these compounds display unusual coupling of magnetic and crystallographic transitions. For instance, magnetic ordering occurs simultaneously with the crystallographic change in Gd$_5$Si$_2$Ge$_2$ [13], ferromagnetic ordering accompanied by a crystal structure rearrangement can be triggered by a magnetic filed in Gd$_5$Ge$_4$ [14], and a pressure-induced magneto-structural coupling is present in Tb$_5$Si$_2$Ge$_2$ [15]. Conversely, the compound Er$_5$Si$_4$ exhibits an interesting decoupling of the magnetic and structural transformations [16,17]. The O(I) ↔ M phase transformation temperature in Er$_5$Si$_4$ is extremely sensitive to applied hydrostatic pressure as compared to other known 5:4 compounds [10]. In addition, this structural transition is in the paramagnetic region weakly depends on the applied magnetic field, as observed in both polycrystalline [18] and single-crystalline samples [19].

The identification of crystal structures and the investigation of phase transitions in the R$_5$(Si$_x$Ge$_{1-x}$)$_4$ compounds are often performed using X-ray powder diffraction techniques [14,19–23] since it is well known that these analytical methods are capable

of quick and accurate material characterization. The most common use of powder diffraction is in the identification and characterization of crystalline solids including the concentration and crystal structure of phases present in a sample. In order to obtain the most accurate results, all potential factors that may affect the reliability in the phase amounts calculation should be closely examined.

A series of experiments described in this article were designed to study how differences in sample preparation may affect the reported results of the X-ray diffraction studies of an Er_5Si_4 alloy. In this study the duration of grinding time used to produce samples for powder diffraction was varied as well as the type of X-ray diffractometer used. The effect these differences have on determined phase concentrations is presented and discussed.

2. Experimental details

An Er_5Si_4 alloy (Er_5Si_4 #1) was prepared by arc-melting stoichiometric amounts of Er (99.98 wt.%) and Si (99.9995 wt.%) on a water-cooled copper hearth under an argon atmosphere. The button was re-melted six times to ensure homogeneity. The microstructure of this alloy was examined using a JEOL 6060LV scanning electron microscope equipped with an X-ray energy dispersive spectrometer.

The arc-melted Er_5Si_4 button was sectioned and a piece weighting 1.566 g was ground into powder with an agate mortar and pestle in an argon atmosphere glove box. The resultant powder was screened using a clean sieve having openings of 38 μm, and approximately one quarter of the uniformly mixed powder was separated from the total amount and divided evenly into three parts suitable for conventional X-ray powder diffraction (XRD), synchrotron high resolution powder diffraction (HRPD), and particle size measurements. The remaining powder was then ground for an additional 20 min, after which one third was again separated and divided into equal portions for conventional XRD, HRPD and particle size measurements. This basic process was then repeated two more times, producing a series of samples. The only difference between these samples is the length of grinding time to which the particles had been subjected. A flow chart of the entire procedure is shown in Fig. 1. The particle sizes of all powders were measured using a Micro-Trac S3500 particle analyzer employing light scattering technology.

Conventional X-ray powder diffraction (XRD) studies were carried out on a PANalytical X'Pert PRO diffractometer using monochromatic Cu Kα$_1$ radiation at ambient temperature. The Bragg–Brentano reflection geometry was used. The X-ray diffraction patterns covered a 2θ range 20–120° with a step of 0.01675°. High resolution X-ray powder diffractions (HRPD) with transmission geometry and employing a synchrotron source were performed at Argonne National Laboratory [24]. The mean operating wavelength for this source is 0.4138 Å. Multiple point detectors were used for automatic data collection. The diffraction data were collected continuously from 0.5° to 50° with a scan speed of 0.01 deg/s and spaced at 0.001°. The sample powders were coated on the inner walls of Kapton tubes that

were rotated during the scan at a rate of ∼5000 rpm. The collected diffraction data using both conventional laboratory Cu Kα$_1$ radiation and a synchrotron source were quantitatively analyzed by the Rietveld method using LHPM RIETICA [25].

In order to study the effect of low temperature anneals on the XRD results of the ground powders, another Er_5Si_4 alloy, designated "Er_5Si_4 #2", was prepared in the same way as "Er_5Si_4 #1". A sample weighing ∼1.5 g was separated from the "Er_5Si_4 #2" alloy and ground into powder in an argon atmosphere glove box and screened with a sieve having openings of 38 μm. A small amount of powder (named "38 μm sieved") used as a control was extracted: one part was used for an initial XRD experiment while the rest was separated for anneals. The remaining powder was then ground for an additional 60 min (named "+60 min"). Again, a small part of the resultant powder was taken for conventional XRD, and the remainder was used for annealing experiments.

The annealing was performed as follows: the powders were wrapped in tantalum foil and sealed in a quartz tube which was evacuated and then filled with helium. Several pieces of pure yttrium metal were also inserted into the tube to act as oxygen getters. The sealed quartz tubes were annealed at 500 °C for 20 min and air cooled. The annealed powders were then examined with conventional XRD.

3. Experimental results

3.1. Scanning electron microscopy

The microstructure of the first Er_5Si_4 alloy in the as-cast state is shown in Fig. 2. The morphology of one random area of the polished and ion-etched sample surface imaged with secondary electrons (SE) is shown in Fig. 2a, while the corresponding image using backscattered electrons (BSE) is shown in Fig. 2b. The atomic number sensitivity of BSE imaging produces contrast that indicates the existence of four phases, namely, a black phase, two grey phases of different shades, and a series of thin linear features growing in specific directions that appear white. Combined with EDS analysis (Table 1), the black phase is identified as ErSi (i.e. the 1:1 phase), and the two grey phases (light-grey matrix marked "L" and dark-grey grain marked "D") have the same composition of Er_5Si_4 (i.e. the 5:4 phase). There are two possible reasons for the gray areas having the same composition but different contrast, both related to the complex crystallography of Er_5Si_4. As discussed in [26], the dark-grey grain may be exactly the same phase as the light-grey matrix, only possessing a slightly different orientation. Another possibility is that the observed contrast is due to the presence of the monoclinic 5:4 phase, which has a slightly different crystal structure from that of the orthorhombic 5:4 matrix. This small difference could be sufficient to alter the coefficient of back scattering associated with each region due to the electron channeling effect [27], producing a slight contrast between two structures.

A reliable composition from the white linear features is difficult to obtain using EDS in SEM due to their narrow size. Spreading of the incident electron beam due to interactions with the sample as predicted using Monte Carlo simulations [28] shows that any composition detected will actually be a combination of the matrix and the white features. However, based on previous research results [29,30] we believe the linear features are Er_5Si_3, (i.e. the 5:3 plates).

3.2. Powder size measurement

It is logical to assume that extending the length of mechanical grinding time should result in a continuing decrease of average particle size. This was confirmed by the particle size measurements. For convenience, the initial sieved powder is designated "Er_5Si_4 −38 μm" in this article, with the other three powder samples being named "Er_5Si_4 +20", "Er_5Si_4 +40" and "Er_5Si_4 +60" to denote that the grinding time was extended by 20, 40 and 60 additional minutes. The measured median particle size of these four powder samples using the MicroTrac are 11.9, 6.7, 4.2, and 3.0 μm, respectively. Although the median sizes of the powders were measured, it is safe to suggest that the change of the median size reflects that of the average size, and they both have the same variation trend. The distribution in powder sizes as denoted by the
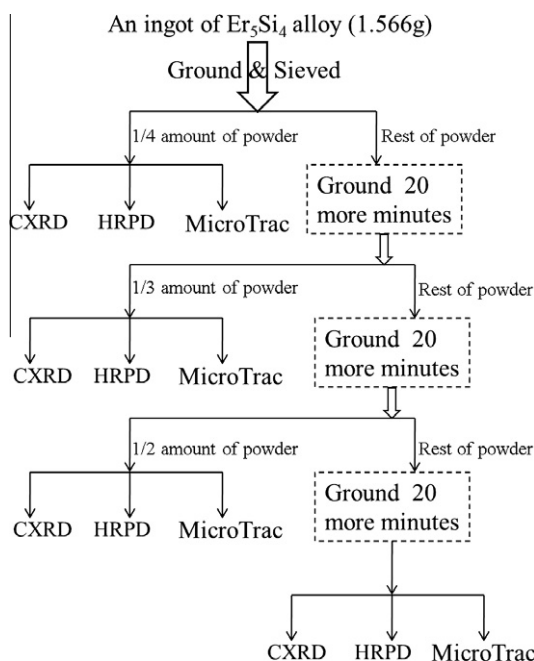

Fig. 1. Flow chart showing powder sample preparation and handling for Er_5Si_4 #1.