A new amorphous spin glass material: $Fe_3(SbTe_3)_2$

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Abstract

A new material, $Fe_3(SbTe_3)_2$, is prepared by using a rapid precipitation metathesis reaction between the Zintl material K_3SbTe_3 and $FeCl_2$ in solution. The d.c. electrical conductivity of this material exhibits metallic conductivity. The magnetic behavior of $Fe_3(SbTe_3)_2$ is characterized as a spin glass with a freezing temperature of 4.0 K. Magnetization data are reported as thermal remanent magnetization and isothermal remanent magnetization as a function of both magnetizing field and temperature.

Introduction

The metathesis of several types of Zintl phases with metal salts in solution has been shown to produce amorphous intermetallic solids [1, 2]. Because of rapid precipitation of the intermetallic product, the materials have an amorphous structure. Although most amorphous solids are prepared by rapid thermal quenching, pyrolytic or sputtering techniques, chemical methods of producing intermetallic solds are also a valuable tool. We have previously reported the magnetic properties of intermetallic materials of the general formula M_2SnTe_4 [1] and $M_5(InTe_4)_2$ [2], where M is a transition metal (e.g. Cr, Mn, Fe, Co and Ni). These intermetallic materials may be prepared because of the differences in the electronegativities of the elements that comprise the precursor Zintl phase material. This electronegativity difference gives rise to a great deal of ionic character in the Zintl phase, and the ionic character may be sufficient to allow the solvation of Zintl ions in polar solvents. The intermetallic material forms from the reaction of the electron rich Zintl anions with transition metal cations. These new intermetallic materials exhibit some remarkable properties including specific resistivity ranging from 10^4 to 10^{-4} Ω cm and a spin glass transition at temperature ranging from 4 to 20 K.

Many of the intermetallics that we have reported have exhibited spin glass behavior. The spin glass phenomenon has been extensively studied for the past two decades. The spin glass state is characterized by some very unusual behavior in the bulk magnetic properties of the materials. There are several reviews that discuss the theory and concept of the spin glass phenomenon, as well as the many reports of experimental studies on spin glasses [3].

We have recently synthesized two new ternary Zintl compounds composed of elements from Groups I–V–VI of the periodic table, K_3SbTe_3 [4] and $LiSbTe_2$ [5]. These Zintl phases were prepared from the direct combination of the elements at high temperatures. Although the $LiSbTe_2$ compound is found to be insoluble in all polar solvents because of increased covalency in the crystalline lattice, the K_3SbTe_3 analog forms solutions with DMSO, DMF, formamide, ethylenediamine and H_2O solvents, and therefore shows promise for preparation of intermetallic solids via the metathesis procedure. In this report, we describe the synthesis and characterization of the electrical and magnetic properties of a new amorphous, intermetallic material $Fe_3(SbTe_3)_2$. This material is prepared by using the rapid pricipitation metathesis reaction between the Zintl material K_3SbTe_3 and $FeCl_2$.

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Experimental

Syntheses

Due to the air sensitivity of the materials used in this reaction, all manipulations were carried out in an argon-filled glovebox containing less than 1 ppm of oxygen.

K_3SbTe_3

The ternary Zintl material K_3SbTe_3 was prepared as described previously [4].

$Fe_3(SbTe_3)_2$

The transition metal compound was prepared by the reaction of an aqueous solution of K_3SbTe_3 and $FeCl_2$. In a typical preparation, a stoichiometric quantity of K_3SbTe_3 solution (50 ml, 0.03 M) was slowly added to $FeCl_2$ solution (20 ml, 0.05 M) while stirring. A fine black precipitate was immediately formed, separated by suction filtration, washed with water and acetone, and dried overnight under vacuum.

Magnetism

The magnetic susceptibility and magnetization were measured on a SHE Corp. VTS-50 superconducting SQUID susceptometer, interfaced to an IBM-XT computer system. Measurement and calibration techniques have been reported elsewhere [6]. Two types of experiments were conducted: magnetic susceptibility (M/H) as a function of temperature, and remanent magnetizations as a function of field. In the magnetic susceptibility measurement, two different procedures were used: (i) zero field cooling, where the sample was slowly cooled in zero field to a temperature of 2.2 K at which the measuring field of 1.0 kG was switched on, and the magnetization was measured as a function of temperature, (ii) field cooling where the field (1.0 kG) was turned on at a temperature well above the freezing temperature. In the remanent magnetization measurement, both thermal remanent magnetization (TRM) curves and isothermal remanent magnetization (IRM) were obtained as a function of field. The TRM experiment involves slowly cooling the sample in an applied magnetic field to a measuring temperature below the freezing temperature and then switching off the field and measuring the remanent magnetization after a specified elapsed time. On the other hand, IRM data are obtained by cooling the sample to the measurement temperature in zero field, applying a field for a certain time and then switching off the field and measuring the remanent magnetization after a specified elapsed time.

Resistivity measurements

Resistivity measurements on pressed pellets were made using a four-probe van der Pauw method [7]. The current was supplied by a Keithley model 224 programmable current source and the voltage drop across the sample was measured using a Keithley model 181 digital nanovoltmeter.

Results and discussion

Amorphous intermetallics that contain magnetic transition metals are good candidates for showing spin glass behavior because they intrinsically possess disorder in the orientations and interactions of the spins. The new amorphous intermetallic is prepared by using the same rapid precipitation metathesis procedure that we have employed to prepare other types of intermetallic solids. An ORTEP diagram of the unit cell of the precursor Zintl phase material, K_3SbTe_3, is illustrated in Fig. 1. The structure consists of an ionic lattice of K^+ cations and discrete $[SbTe_3]^{3-}$ Zintl anions. The ionic character of K_3SbTe_3 permits the Zintl phase to form an ionic solution in polar solvents. It is reported in the Fe_2SnTe_4 intermetallic analog that the tetrahedral structure of the $SnTe_4$ unit that comprises the Zintl anion remains intact when the intermetallic solid is formed. Therefore we expect the $Fe_3(SbTe_3)_2$ solid to contain intact $SbTe_3$ pyramidal units.

The magnetic susceptibility data of $Fe_3(SbTe_3)_2$ were measured over the 2.2 to 300 K temperature region. The measured data are illustrated in Fig. 2 as inverse susceptibility plotted as a function of temperature. At temperatures above 10 K, the inverse magnetic sus-

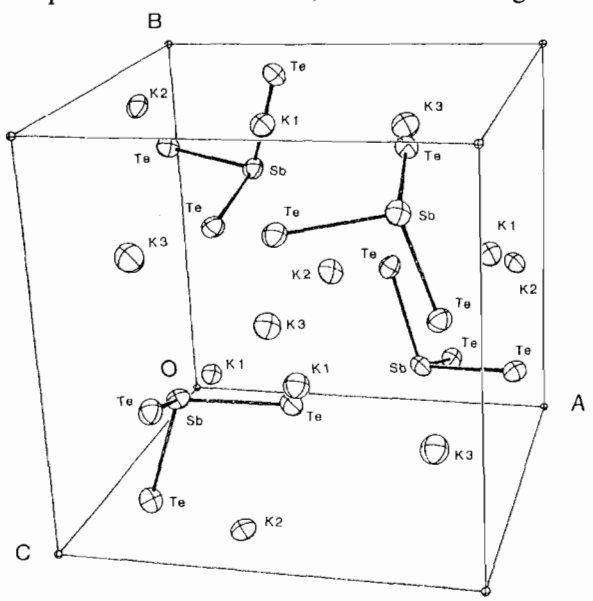

Fig. 1. ORTEP diafram of the unit cell of K_3SbTe_3 showing the $SbTe_3$ trigonal pyramids.

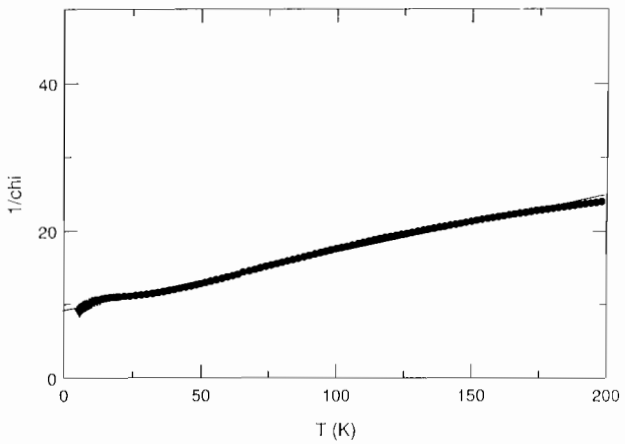

Fig. 2. The inverse magnetic susceptibility of $Fe_3(SbTe_3)_2$ plotted as a function of temperature over the 6 to 200 K temperature region.

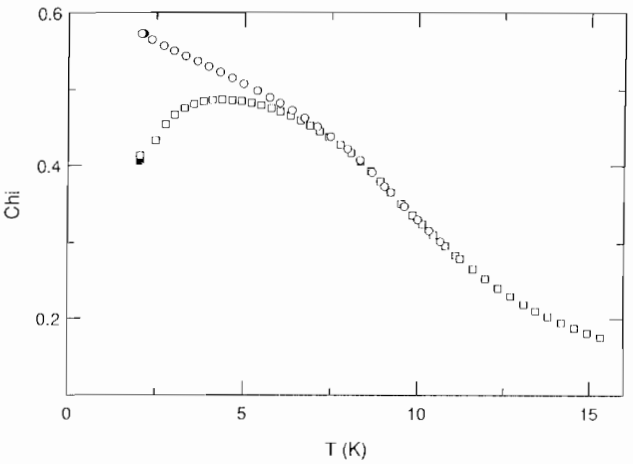

Fig. 3. Plot of the magnetic susceptibility as a function of temperature measured over the 2–15 K temperature region and at a field of 1 kG (□, zero field cooling; ○, field cooling).

ceptibility data exhibit linear behavior consistent with the Curie Weiss equation ($\chi = C/(T-\theta)$). The data were fit to this equation to give a large antiferromagnetic Weiss constant, $\theta = -119.4$ K, and the Curie constant $C = 12.74$ emu K/mol. The large negative value of θ indicates the presence of a significant amount of antiferromagnetic coupling between the unpaired spins on the Fe atoms.

At lower temperatures the $Fe_3(SbTe_3)_2$ sample exhibits anomalous temperature dependent magnetic behavior and also shows a dramatic dependence on cooling condition. Figure 3 illustrates plots of the temperature dependent magnetic susceptibility of $Fe_3(SbTe_3)_2$ for field cooled and zero field cooled experiments. The cusp in the zero field cooled magnetic susceptibility data is strong evidence that $Fe_3(SbTe_3)_2$ exists in a spin glass state with a freezing temperature of about 4 K.

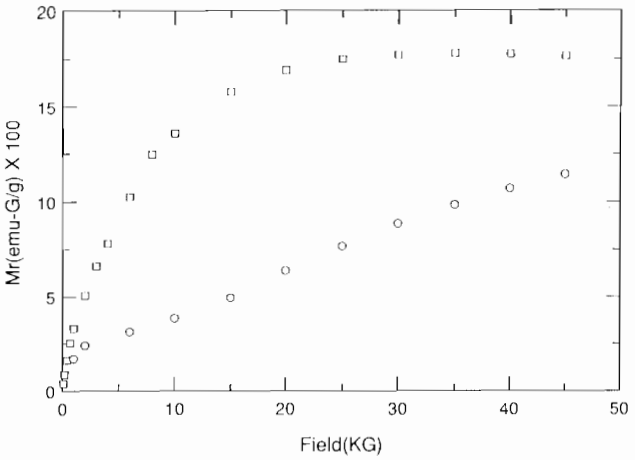

Fig. 4. The thermal remanent magnetization (□) and isothermal remanent magnetization (○) of $Fe_3(SbTe_3)_2$ measured at 2.2 K and plotted as a function of remanent inducing magnetic field at a temperature of 2.2 K.

The most diagnostic experiment for the characterization of the spin glass state is the analysis of the field dependence of the isothermal remanent magnetization (IRM) and thermal remanent magnetization (TRM). At low remanent inducing magnetic fields, the TRM has a large remanent relative to the IRM. These characteristics have been observed in many other spin glass materials [8]. The results of these experiments on $Fe_3(SbTe_3)_2$ are illustrated in Fig. 4. A hump in the TRM curve has been observed in many spin glasses and is characteristic of the spin glass state. Such a hump is apparent in the field dependent plot of the TRM data in Fig. 4. Both IRM and TRM data curves converge to the same saturation remanent at higher magnetic fields because of the increasing importance of short range correlations that destroy the spin glass state.

The results of resistivity measurements using the four-probe van der Pauw method show that the material has metallic behavior at room temperature, with a specific resistivity of $\rho = 2.6 \times 10^{-3}$ Ω cm.

Conclusions

The new amorphous material $Fe_3(SbTe_3)_2$ has been prepared by using rapid precipitation of $SbTe_3^{3-}$ anions and divalent iron(II) cations in solution. This material undergoes a transition to the spin glass state at $T_f = 4.0$ K and also exhibits metallic conductivity at room temperature.

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