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Magnetic and magnetocaloric properties of GdB_2 compound

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In this study, magnetic and magnetocaloric properties of GdB_2 compound were first time investigated.GdB_2 compound was prepared by arc-melting method. The magnetic characterizations of the samples were defined at various temperatures and magnetic fields. Saturation magnetization value is 19.5 emu/g at 275 K. The magnetic entropy change of the GdB_2 compound was calculated from the isothermal magnetization curves under the different magnetic fields. The peak value of $|\Delta S_m|$ is 1.89 J/kg K under the applied field changing from 0 T to 4 T. The adiabatic temperature change was calculated from heat capacity. The peak value of ΔT_{ad} is 0.49 K at 1 T magnetic field.

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1. Introduction

Magnetic refrigeration based on magnetocaloric effect is becoming a promising technology to replace the conventional gas-compression expansion technique. Compared with gas refrigerators, magnetic refrigerators have a number of advantages such as high energy efficiency, small volume and ecological cleanliness. Nowadays, nearly all the studies on magnetocaloric effect and magnetic cooling have been focused on the search and find the most suitable magnetic materials which technologically viable in magnetic refrigeration technology. Therefore, the magnetic materials that show a large MCE around room temperature in low magnetic fields are especially desirable. Up to now, a variety of near room temperature magnetic refrigeration materials based on first-order and second-order magnetic phase transitions such as $Gd_5Si_{4-x}Ge_x$ [1], MnAs [2] , $MnFeP_{1-x}As_x$ [3], $MnAs_{1-x}Sb_x$ [4], $LaFe_{13-x}Si_x$ [5], amorphous alloys [6] and some perovskites [7-9] have been extensively investigated. The materials showing first-order magnetic phase transition have showed that they undergo a simultaneous structural and magnetic phase transition, which leads to a giant magnetic entropy change as large as 20-30 J/kg.K for a magnetic field change of 0-5 T across its ordering temperature. Unfortunately, as discussed by Wang et al [10], a first order transition is always associated with thermal or field hysteresis. This hysteresis may result in a reduced efficiency of the refrigeration cycle as it may be considered as a dead loop. This will be especially of importance if one wants to work in a low magnetic field. Although the materials showing second-order phase transition have generally showed small magnetic entropy change than that of the materials showing first-order magnetic phase transition, gadolinium is one of the most broadly studied magnetic refrigerant materials based on a second-order magnetic phase transition due to the above mentioned reason and many advantages such as easy forming performance and large cooling power in comparison with above mentioned compounds. Another important reason is that Gd is known to have the largest magnetocaloric effect near room temperature [10]. Therefore, Gadolinium is the best material available today for magnetic refrigeration near room temperature. Unfortunately, the low strength and easy deformation of Gd limits its practical application [11]. In order to strengthen Gd and to search for other candidate possessing qualities as good as Gd, many binary Gd-R (R= other rare earth such as Ho, Tb, Dy, B and Y) alloys have been studied [10, 12, 13]. The magnetic and magnetocaloric properties of $Gd_{1-x}B_x$ alloys for small quantity of B (x = 0.02, 0.05, 0.06, 0.07, 0.09 and 0.12) were detailed investigated by Wang et al [14] and Min et al [15]. In this study, magnetic and magnetocaloric properties of GdB_2 compound have been investigated in detail.

2. Experimental

Polycrystalline sample of GdB_2 was prepared by arc melting the raw materials in a water-cooled copper crucible under high-purity argon atmosphere. The purity of the starting elements was 99.99 % for Gd and 99.9+ % for B. The sample was turned over and re-melted at least four times to ensure homogeneity. No further heat treatment was performed. The structures of the samples were investigated by X-ray diffractometer (Rigaku-Radb) system. X-ray diffractograms were recorded with a power diffractometer at room temperature using CuKα radiation. The magnetic measurements were performed using a Q-3398 (Cryogenic) magnetometer in a temperature range from 50 to 250 K and 6 T maximum magnetic field was applied. The specific heat of the sample was measured by using a Physical Properties Measurement System (PPMS) dc extraction magnetometer by Quantum Design Corporation.

2. Results and discussion

Fig. 1 shows the room temperature X-ray diffraction patterns of GdB_2 compound and pure Gd. The X-ray diffraction patterns show that GdB_2 compound crystallized in a single phase of hexagonal structure belonging to space group P6/mmm.

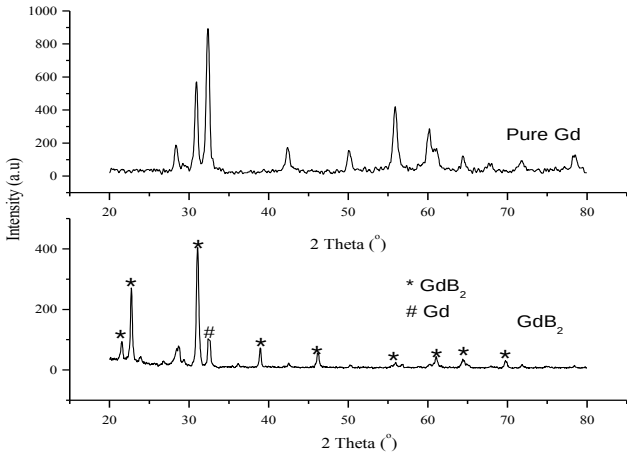

Fig. 1. XRD patterns of GdB_2 compound and pure Gd at room temperature.

Fig. 2 shows the temperature dependence of magnetization for GdB_2 compound measured in an applied magnetic field of 0.1 T. The Curie temperatures, T_c, defined as the temperature of the maximum value in |dM/dT|, were measured to be 299 K at 5 mT magnetic field. The results have showed that with B introduced in Gd, T_c slightly increases from 294 K for pure Gd to 299 K for GdB_2 compound.

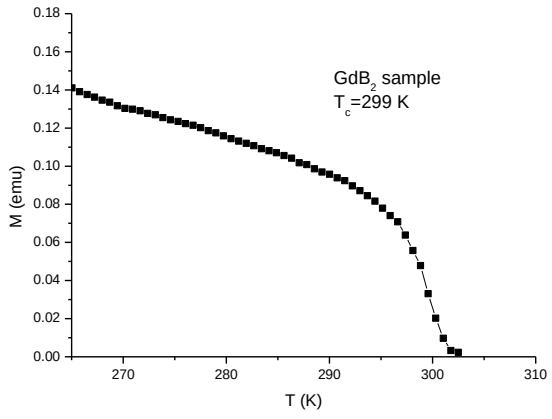

Fig. 2. The temperature dependence of magnetization for GdB_2 compound measured in an applied magnetic field of 0.1 T.

Fig. 3 shows the variation of magnetization as a function of applied magnetic field at different temperatures for GdB_2 compound. The sample shows ferromagnetic like behaviours below the Curie temperature. While the saturation magnetization value is 112 emu/g for pure Gd at 275 K in an applied field of 2.5 T, for the GdB_2 compound the saturation magnetization value has determined as 19.5 emu/g at the same conditions. It is clearly seen that the saturation magnetization value of GdB_2 compound is very small than that of the pure Gd. As it is known, the metal gadolinium belongs to the lanthanide group and crystallizes in the hcp structure with the lattice constant a = 3.629 °A and c/a = 1.597 [16]. The unique electronic and magnetic properties of gadolinium result from the partially filled 4f shell. Gadolinium is a ferromagnet with localized magnetic moments (Heisenberg ferromagnet), where the half filled 4f shell (S=7/2, L=0) gives rise to the large localized magnetic moments of 7 μB per lattice site. It is clear that the increase of non magnetic B content in Gd causes a decrease of total magnetic moment per formula unit. The considerable decrease of saturation magnetization in GdB_2 compound could be attributed the dilution of Gd atoms which have large localized magnetic moments. The decrease in saturation magnetization with increasing B content is in agreement with literature [14, 15].

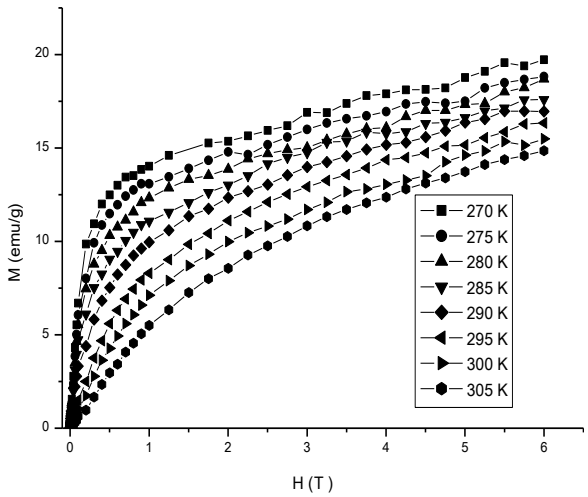

Fig. 3. Isothermal magnetization curves of GdB_2 compound at various temperatures.

The magnetic entropy, which is associated with the MC effect, can be calculated from the isothermal magnetization curves (Fig. 3) under the influence of a magnetic field. According to the classical thermo dynamical theory, the magnetic entropy change ΔS_m produced by the variation of a magnetic field from 0 to H_{max} is given by:

$$\Delta S_m(T,H) = \int_0^{H_{\max}} \left(\frac{\partial M}{\partial T}\right)_H dH \qquad (1)$$

To evaluate the magnetic entropy change ΔS_m numerical approximation of the integral in Eq. (1) is required. The usual method is to use isothermal magnetization measurement at small discrete field intervals and than ΔS_m can be approximated from Eq. (1) by:

$$|\Delta S_m| = \sum_i \frac{M_i - M_{i+1}}{T_{i+1} - T_i} \Delta H \qquad (2)$$

where M_i and M_{i+1} are the experimental values of the magnetization at T_i and T_{i+1} respectively. Using Eq. (2) and experimental M-H curves at various temperatures, the magnetic entropy change with the magnetic field variation can be calculated. Fig. 4 shows the magnetic entropy change at various magnetic fields for the GdB_2 compound. The peak values of entropy change for GdB_2 compound was observed at higher temperature than that of the pure Gd. The peak value of $|\Delta S_m|$ is 1.89 J/kg K at 4 T magnetic field for GdB_2 compound. Generally, the peak temperature of entropy change increases linearly with increasing magnetic field. However, for GdB_2 compound the peak temperatures are nearly unchanged with increasing magnetic field at low (< 2 T) and high (> 2 T) magnetic fields. At 2 T magnetic field a sudden increase is observed in peak temperatures. It was interpreted that this anomalous variation in peak temperature could be existence of some pure Gd in samples or due to the measurements were performed at intervals by 5 Tesla.

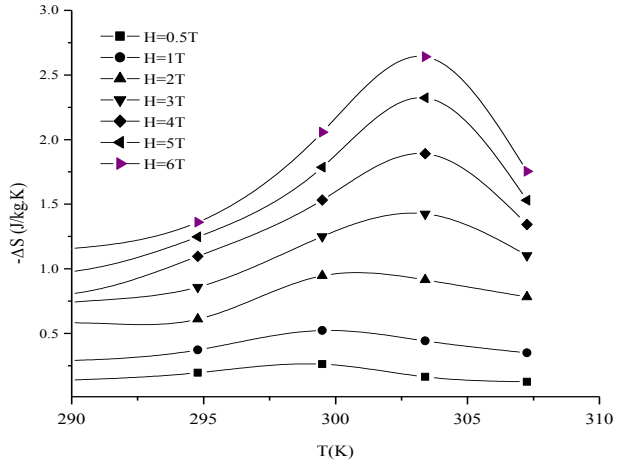

Fig. 4. Magnetic entropy change of GdB_2 compound at various magnetic fields.

Fig. 5 shows the adiabatic temperature change calculated from heat capacity. The inset in Fig. 5 shows the temperature dependence of specific heat of GdB_2 compound at 1 T magnetic field in the vicinity of phase transition. A broad peak observed at 299 K, corresponding to ferromagnetic-paramagnetic transition, in agreement with magnetic data. An approximate estimation of adiabatic temperature change ΔT_{ad} of this sample (Fig. 5) has been performed from the measured $|\Delta S_m|$ and specific heat data using the expression

$$\Delta T_{ad}(T,H) = -\frac{T}{C(T,H)_H} \Delta S_M(T,H) \qquad (3)$$

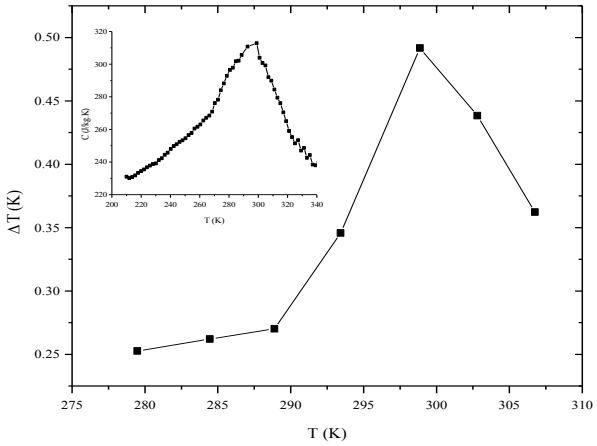

Fig. 5. Estimated adiabatic temperature change for GdB_2 compound under a field change of 1T. The inset shows the temperature dependence of specific heat of GdB_2 compound at 1 T magnetic field.

The peak value of ΔT_{ad} is 0.49 K at 1 T magnetic field for GdB_2 compound. The magnetic free energy F(M,T) can be expand as a Landau expansion in powers of magnetization M neglecting higher order parts as

$$F(M,T) = \frac{c_1(T)}{2} M^2 + \frac{c_3(T)}{4} M^4 - MH \qquad (4)$$

Here $c_1(T)$ and $c_3(T)$ are called as Landau coefficients and the sign of the $c_3(T)$ of M^4 term determines the type of the magnetic phase transition. The first order phase transition is expected in the case of $c_3(T) < 0$ and the second order phase transition in the case of $c_3(T) > 0$. From the condition of equilibrium $\partial F(M,T)/\partial M = 0$, we obtain

$$H = c_1(T)M + c_3(T)M^3 \qquad (5a)$$

$$\frac{H}{M} = c_1(T) + c_3(T)M^2 \qquad (5b)$$

To determine the type of the magnetic phase transition for GdB_2 compound, the measured data for the M-H isotherms (Fig. 3) were transformed to H/M vs. M^2 a plot which is called Arrot plot, the slope of the resulting curves denotes whether a magnetic transition is of first or second order. It can be deduced that if all the curves have a positive slope, the magnetic transition is second order. On the other hand, if some of the curve shows a negative slope at some point, then the magnetic transition is first order. Fig. 6 shows the Arrot plots of GdB_2 compound. The negative slop in the temperature region 290-305 K is clearly seen in the lower M^2 region, implying that GdB_2 belongs to the materials displaying a first order transition.

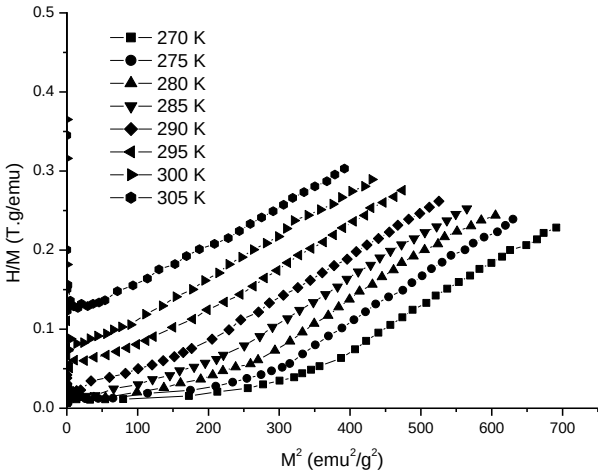

Fig. 6. Arrot plots of GdB_2 compound at various temperatures.

The Landau coefficient $c_3(T)$ could be determined by fitting Eq.(5a) to the magnetic field, H against magnetization M (Fig. 3) or fitting Eq.(5b) to Arrot plot (Fig. 6). Our calculation has showed that $c_3(T)$ is negative (-1.8×10^{-4} Tgr^3/emu^3 at 305 K). According to the theory mentioned above, a negative value of $c_3(T)$ suggest the phase transition in GdB_2 is the first order. The obtained results are in agreement with literature [15]. While the nature of phase transition is first order, the magnetic entropy change is very small. We have interpreted that the main reason of such a small magnetic entropy change in GdB_2 is saturation magnetization. Such a small value in saturation magnetization could cause considerable decrease in magnetic entropy change in GdB_2 compound.

4. Conclusions

The X-ray diffraction patterns showed that GdB_2 compound crystallized in hexagonal structure belonging to space group P6/mmm. The magnetic characterizations of the sample were defined at various temperatures and magnetic fields. The saturation magnetization value of GdB_2 compound is very small than that of the pure Gd. The decrease of saturation magnetization in GdB_2 compound could be attributed the dilution of Gd atoms which have large localized magnetic moments. The Arrot plots showed that GdB_2 compound has first order magnetic phase transition. The peak value of $|\Delta S_m|$ is 1.89 J/kg K under the applied field changing from 0 T to 4 T. The small value of magnetic entropy change attributed to considerable decrease in saturation magnetisation in GdB_2 compound.

Acknowledgements

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