Journal of Solid State Chemistry 258 (2018) 201–211

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Structural and magnetic properties of Fe_2P-type R_6TTe_2 compounds (R = Tb, Dy, Ho, Er, T = Fe, Co, Ru): Magnetic properties and specific features of magnetic entropy change

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ARTICLE INFO

Keywords:
Rare earth compounds
Magnetic properties
Magnetocaloric effect
Heat capacity
Magnetic entropy change

ABSTRACT

The magnetic properties and magnetic entropy changes of the Fe_2P-type Ho_6FeTe_2, Ho_6CoTe_2, Er_6CoTe_2, Tb_6RuTe_2, Dy_6RuTe_2 and Ho_6RuTe_2 (space group P-62m, N 189, $hP9$) have been studied by means of bulk magnetization and heat capacity measurements. Also, the tentative magnetic entropy change $\Delta S_m^* = (\partial M / \partial T) \times H$ was used for characterization of magnetic ordering.

Ho_6FeTe_2, Ho_6CoTe_2, Er_6CoTe_2, Tb_6RuTe_2, Dy_6RuTe_2 and Ho_6RuTe_2 exhibit complex field sensitive ferro-antiferromagnetic ordering. The correlation between the isothermal magnetic entropy change and the magnetic ordering of these compounds have been studied.

1. Introduction

Intermetallic compounds composed of rare earth, transition metal and p-elements are being actively studied for the occurrence of large magnetocaloric effect over suitable temperature ranges for applications in magnetic refrigeration/heating technologies and for the occurrence of giant coercive force as potential basis for permanent magnets. Meanwhile, it is necessary to know specific features of crystal structure and magnetic properties of rare earth compounds in details to reach an optimum of their magnetic properties.

The Tb_6RuTe_2 [1], Dy_6RuTe_2 [1–3], Ho_6RuTe_2 [1–3], Ho_6FeTe_2 [1,2,4], Ho_6CoTe_2 and Er_6CoTe_2 [1,2,5] compounds belong to the family of Fe_2P-type R_6TX_2 rare earth compounds (R = Sc, Y, Gd – Tm, T = Mn, Fe, Co, Ni, Ru; X = Sb, Bi, Te; space group P-62m, No. 189, $hP9$) [1–16].

These compounds are formed by a diffusion method and from structural point of view they are ordered variant of Mg-type rare earth based solid solutions: transition metal T and p-element X are inserted into Mg-type rare earth lattice R with formation of Fe_2P-type R_6TX_2 compounds with anisotropic distortion of initial Mg-type rare earth lattice as shown in Ref. [3]. Thus, Fe_2P-type R_6TX_2 compounds may be viewed as one of the variants for the magnetic property modification of the initial rare earths.

The distortion of Mg-type sublattice by the transition metal and p-element leads to considerable change of magnetic ordering of the rare earth sublattice in the resulting R_6TX_2 compounds. The magnetic ordering of transition metal sublattice T was not detected via neutron diffraction study in zero applied field in R_6TX_2 compounds [3–5,12–16], meanwhile Mn-containing compounds exhibit strong increase in temperature of magnetic ordering in comparison with Fe-, Co-, Ni- and Ru-containing R_6TX_2 compounds. Ho_6FeBi_2 and Ho_6CoBi_2 show Curie temperatures of 54 K and 70 K, respectively, whereas Curie temperature of Ho_6MnBi_2 is 200 K [3,13]. The compounds Ho_6RuTe_2, Ho_6FeTe_2 and Ho_6CoTe_2 exhibit magnetic ordering at 11 K, 24 K and 60 K, respectively, while Ho_6MnTe_2 show magnetic ordering at T_C = 153 K [3–5,17]. These results suggest that the magnetic ordering of Mn sublattice facilitates the magnetic ordering of rare earth sublattice in the R_6TX_2 compounds.

Thus, Fe_2P-type R_6TX_2 compounds and their solid solutions permit one to engineer magnetic material with different magnetic ordering temperatures over a large temperature range and the magnetic entropy change indicates the magnetocaloric effect and field induced transformation of magnetic ordering of rare earth compounds.

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http://dx.doi.org/10.1016/j.jssc.2017.10.023
Received 3 July 2017; Received in revised form 5 September 2017; Accepted 16 October 2017

To understand variants ordering of rare earth sublattice and magnetic field-induced transitions in Fe_2P-type compounds and to understand the role of magnetic entropy change for characterization of magnetic ordering, the magnetic properties, magnetocaloric effect, heat capacity and magnetic entropy change of Ho_6FeTe_2, Ho_6CoTe_2, Er_6CoTe_2 and $\{Tb, Dy, Ho\}_6RuTe_2$ compounds have been investigated in this work.

2. Experimental details

The Ho_6FeTe_2, Ho_6CoTe_2, Er_6CoTe_2 and $\{Tb, Dy, Ho\}_6RuTe_2$ alloys were prepared by arc-furnace melting of stoichiometric amounts of rare earth (99.9 wt%), Fe, Co and Ru (99.95 wt%) and Te (99.99 wt%) with some surplus tellurium for compensation of the weight loss. The samples were annealed at 1070 K for 240 h in an argon atmosphere and subsequently quenched in ice-cold water. The quality of the samples was evaluated using powder X-ray diffraction and microprobe analyses. The X-ray data were obtained on a Rigaku D/MAX-2500 diffractometers (Cu K_α radiation, $2\theta = 10$–$80°$ and $2\theta = 5$–$120°$, step 0.02). An INCA-Energy-350 X-ray EDS spectrometer (Oxford Instruments) on the Jeol JSM-6480LV scanning electron microscope (20 kV accelerating voltage, beam current 0.7 nA and beam diameter 50 μm) was employed to perform the microprobe analysis of the sample. Signals averaged over three points per phase estimated standard deviations of 1 at% for rare earth (measured by L-series lines), 1 at% for iron, cobalt, ruthenium and tellurium (measured by K-series lines).

Magnetization measurements of bulk polycrystalline $Ho_6\{Fe, Co\}Te_2$, Er_6CoTe_2 and $\{Tb, Dy, Ho\}_6RuTe_2$ were carried out using a vibrating sample magnetometer (VSM attachment on PPMS Dynacool System, USA) in the temperature range of 2–300 K and in magnetic fields up to 140 kOe. Specific heat measurements were performed using relaxation method in PPMS. Low field (100 Oe) magnetization data were obtained in zero-field-cooled (zfc) and field-cooled (fc) states to determine the magnetic ordering temperatures. The Curie temperature (T_C) was defined as the dM/dT minima, and Néel temperature (T_N) was defined as M maximum. The temperature of transformation of the magnetic ordering T_m or spin-reorientation transition T_{SR} was defined as local dM/dT minima or M maximum of the thermal magnetization curve. Magnetization as a function of temperature was measured in 5 kOe field in zero-field-cooled state to obtain effective paramagnetic moment and paramagnetic Weiss temperature. Magnetization vs field hysteresis curves were recorded at different temperatures to obtain magnetization in field of 140 kOe ($M_{140\ kOe}$), remanent magnetization (M_{res}), critical (H_{crit}) and coercive fields (H_{coer}). Magnetization isotherms were obtained at various temperatures with a temperature step of 5 K (or 4 K) and a field step of 2.5 kOe to calculate isothermal magnetic entropy changes (ΔS_m).

3. Theory and calculations

The unit cell data were derived from powder XRD using the Rietan-program [18,19] in the isotropic approximation at room temperature. Bilbao Crystallographic server [20] was used for analysis of Fe_2P-type structure [2] according to the symmetry tables of the International Tables of crystallography [21]. The paramagnetic susceptibility was fitted to the Curie-Weiss law, yielding the effective magnetic moments and paramagnetic Weiss temperatures [22]. Magnetic field (H), coercive field (H_{coer}) and critical field (H_{crit}) are given in Oe unit (1 Oe = $10^3/4\pi$ A/m and magnetic field of 1 Oe corresponds to the strength of a magnetic field of 10^{-4} T). Magnetization is given in emu/g and μ_B units (1 emu/g = 1 A m^2/kg, 1 $\mu_B = 9.7400968(20) \cdot 10^{-24}$ A m^2) [22].

Magnetocaloric effect (MCE) is calculated in terms of the isothermal magnetic entropy change, ΔS_m, using the magnetization vs field data obtained near the magnetic transition using the thermodynamic Maxwell relation [23]. The relative cooling power in field change 0–50 kOe ($RCP_{50\ kOe}$) is calculated by multiplying of maximum of the ΔS_m by the full ΔT width at half maximum of ΔS_m. The tentative magnetic entropy change ΔS_m* was calculated as $\Delta S_m^* = (\partial M / \partial T) \times H$ from magnetization vs temperature in field of 100 Oe and 5 kOe (here H the applied magnetic field, T the temperature and M the magnetization) [24]. The tentative magnetic entropy change ΔS_m* is same to magnetic entropy change ΔS_m at permanent $\partial M / \partial T$ in different applied magnetic fields and ΔS_m* permits to understand type of magnetic ordering. Electronic heat capacity coefficient γ of Er_6CoTe_2 was calculated by the expression $C_P / T = \gamma + \beta \cdot T^2$ [22] above the magnetic ordering temperature.

4. Results

4.1. Quality of R_6TX_2 samples and unit cell data of Fe_2P-type compounds

The X-ray powder analyses showed that the $Ho_6\{Fe, Co\}Te_2$, Er_6CoTe_2 and $\{Tb, Dy, Ho\}_6RuTe_2$ compounds crystallize in the Fe_2P-type structure

Table 1
Unit cell data of Fe_2P-type R_6TTe_2 (R = Tb, Ho, Er, T = Fe, Co, Ru), space group P-62m, N 189, hP9, Z = 1, atomic positions: R1 3g [x_{R1}, 0, 1/2], R2 3f [x_{R2}, 0, 0], T 1b [0, 0, 1/2], Te 2c [1/3, 2/3, 0].

N	Compound	*a* (nm)	c (nm)	c/a	V (nm^3)	x_{R1}	x_{R2}	R_F (%)	Ref.
1	Tb_6RuTe_2	0.82973(4)	0.40162(2)	0.48404	0.23945	0.5970(4)	0.2421(4)	5.0	[a]
	Tb_6RuTe_2	0.82979	0.40162	0.48400	0.23949	0.5971	0.2426		[1][b]
2	Dy_6RuTe_2	0.82515(5)	0.40077(2)	0.48569	0.23632	0.5971(5)	0.2442(4)	5.3	[a]
	Dy_6RuTe_2	0.82449	0.40049	0.48574	0.23577	0.5978	0.2430		[1][c]
3	Ho_6RuTe_2	0.82193(3)	0.39982(2)	0.48644	0.23392	0.6011(3)	0.2424(3)	2.6	[a]
	Ho_6RuTe_2	0.82106	0.39943	0.48648	0.23320	0.6015	0.2419		[1][d]
4	Ho_6FeTe_2	0.82017(4)	0.40003(2)	0.48774	0.23304	0.6000(5)	0.2379(4)	4.3	[a]
	Ho_6FeTe_2	0.81894	0.39939	0.48769	0.23197	0.5997	0.2386		[1][e]
5	Ho_6CoTe_2	0.82348(2)	0.39360(1)	0.47797	0.23115	0.6000(3)	0.2379(3)	3.4	[a]
	Ho_6CoTe_2	0.82328	0.39352	0.47799	0.23099	0.6001	0.2376		[1][f]
6	Er_6CoTe_2	0.81975(4)	0.39239(2)	0.47867	0.22836	0.5985(4)	0.2365(4)	2.9	[a]
	Er_6CoTe_2	0.81955	0.39232	0.47870	0.22820	0.5981	0.2375		[1][g]

[a] This work.
[b] Tb_6RuTe_2 [1] PDF#00-066-0505.
[c] Dy_6RuTe_2 [1] PDF#00-060-00176.
[d] Ho_6RuTe_2 [1] PDF#00-060-00169.
[e] Ho_6FeTe_2 [1] PDF#00-060-00172.
[f] Ho_6CoTe_2 [1] PDF#00-059-90324.
[g] Er_6CoTe_2 [1] PDF#00-061-10126.