Journal of Alloys and Compounds 680 (2016) 612–616

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Magnetic and magnetocaloric properties of $Gd_6(Mn_{1-x}Co_x)_{23}$ compounds ($x \leq 0.3$)

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ARTICLE INFO

Article history:
Received 7 December 2015
Received in revised form
10 March 2016
Accepted 17 April 2016
Available online 22 April 2016

Keywords:
Lanthanide intermetallic compound
Magnetic properties
Magnetocaloric properties
Magnetic entropy change

ABSTRACT

The magnetic and magnetocaloric properties of the Th_6Mn_{23}-type structure $Gd_6(Mn_{1-x}Co_x)_{23}$ ($x \leq 0.3$) compounds are investigated from DC magnetization measurements. The Curie temperature of these ferrimagnetic materials evolves non-continuously with the Co content from $T_C = 489$ K for $x = 0$ to $T_C = 118$ K for $x = 0.3$. In relation with the lower magnetic moment of Co atoms compared with that of Mn atoms, the Co to Mn substitution leads to a decrease of the maximal magnetization, recorded at 5 K in an applied magnetic field of 9 T, from 54.7 μ_B/f.u. for $x = 0$ to 36.3 μ_B/f.u. for $x = 0.3$. These materials present an anomalous magnetocaloric effect, characterized by two broad $-\Delta S_M$ maxima of moderate magnitude at T_C and around 100 K, yielding to wide magnetocaloric response from T_C down to the lowest temperature, and consequently, a relatively large cooling capacity $q_{10-350K}$ ($\mu_0\Delta H = 5$ T) reaching ~ 3.7 J cm^{-3} for $Gd_6(Mn_{0.875}Co_{0.125})_{23}$. The results are analyzed and discussed in connection with previously published data.

1. Introduction

Research activity for identifying new magnetic materials having magnetocaloric properties suited to potential magnetic refrigeration applications near or below room temperature [1–4] is of increasing interest since the discovery of the giant magnetocaloric effect [5,6]. Part of the present research activity on magnetocaloric effect (MCE) applications is devoted to gas liquefaction technology, especially in view of storage and transportation of emerging fuels (*e.g.* hydrogen, natural gas) [7,8]. Magnetocaloric liquefaction is expected to be more efficient and more ecological than conventional gas-cycle liquefiers. For practical applications materials should display a large magnetocaloric effect (MCE) extending over a significant temperature interval. Moreover, it should be made from cheap, abundant, and non-toxic elements and should be easy to fabricate and to machinate [2,9].

In previous papers, we investigated the magnetocaloric properties of the Th_6Mn_{23}-type R_6Mn_{23} compounds (R = rare-earth element) [10] and some of their derivatives, namely $Gd_{6-x}R_xMn_{23}$ [11] and $Gd_6(Mn_{1-x}Fe_x)_{23}$ [12]. In these ferrimagnetic materials, the R and T (= Mn or Fe) sublattices order magnetically at two different temperatures which can be altered by chemical substitutions. The Mn sublattice orders above 400 K [10]. Fe substitution allows reducing the ordering temperature down to ~100 K in $Gd_6(Mn_{1-x}Fe_x)_{23}$ with x varying from 0.3 to 0.5 [12,13]. The maximum R ordering temperature is as expected observed for R = Gd [10], which has the highest de Gennes factor among the 4f elements, near ~ 100 K. Substituting Gd with another heavy rare-earth element allows displacing the R ordering to lower temperatures [11]. This yields a partially tunable magnetocaloric response of moderate magnitude (<45 mJ cm^{-3} K^{-1} for $\mu_0\Delta H = 5$ T) but which extend over a broad temperature interval, providing thus a relatively high cooling capacity between 10 K and 350 K (for $\mu_0\Delta H = 5$ T) which reaches q = 4.2 J cm^{-3} for Ho_6Mn_{23} [10].

Due to their complex crystal and magnetic structures, the R_6Mn_{23} compounds involving a heavy rare-earth R element have the features to possess a higher magnetization than those involving light rare-earth element [10]. The R_6Mn_{23} (R = Y, Nd, Sm, Gd–Tm, Lu) compounds crystallize in the Th_6Mn_{23}-type structure (space group *Fm-3m*), which comprises one crystallographic site for the R atoms and four sites for the Mn atoms (4b, 24d, $32f_1$, and $32f_2$)

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http://dx.doi.org/10.1016/j.jallcom.2016.04.198

[10,14,15]. From polarized neutron diffraction experiments on Y_6Mn_{23} a collinear ferrimagnetic arrangement has been found due to the antiparallel alignment of the $32f_1$ and $32f_2$ magnetic moments with those of the 4b and 24d sites [16]. The refined Mn moments values at 4.2 K are: ~ −2.8, ~ −2.1, ~ +1.8, and ~ +1.8 μ_B on the 4b, 24d, $32f_1$, and $32f_2$ sites, respectively [16]. Hence, the net magnetization is parallel to the $32f_1$ and $32f_2$ sites magnetic moments. In R_6Mn_{23} compounds involving a heavy rare-earth element, the R magnetic moments couple antiferromagnetically with the less magnetized of the Mn sublattices to form complex non-collinear magnetic structures [16,17]. The (usual) negative sign of the Gd–Mn magnetic exchange has been confirmed by neutron inelastic scattering on Gd_6Mn_{23} [18]. The decrease of both the magnetization and the ordering temperature upon Fe substitution in $Gd_6(Mn_{1-x}Fex)_{23}$ is due to the Fe atoms carrying a lower magnetic moment than the Mn atoms in these phases [12].

In this paper, we focus on the $Gd_6(Mn_{1-x}Co_x)_{23}$ (with $x \leq 0.3$) solid solution with the aim to determine the magnetic and magnetocaloric properties of these compounds and to explore their potential interest for future cooling applications as active and/or passive materials.

2. Experimental details

The $Gd_6(Mn_{1-x}Co_x)_{23}$ compounds with x = 0, 0.01, 0.03, 0.07, 0.1, 0.125, 0.15, 0.2, 0.3 and 0.4 have been synthesized starting from stoichiometric amounts of high-purity elements (Gd 99.9 wt.% from Rhodia, Mn 99.99 wt.% from Cerac and Co 99.8 wt.% from Cerac). The mixtures were melted in a water-cooled copper crucible using a high frequency induction furnace (CELES) under pure argon atmosphere. The samples were not annealed after melting. The purity and chemical composition of each sample have been checked by microprobe analysis (Cameca SX 100) on mirror polished powder samples dispersed in a cold resin. Polishing was performed using SiC paper from 800 to 1200 grit under water, and finished with a 1 μm diamond paste. The purity was evaluated from backscattered electron (BSE) micrographs on different particles and the chemical composition was determined from an average of six pinpoints randomly chosen among the sample. The crystallographic structure and the presence of impurities have been verified by powder X-ray diffraction (Philips X'Pert Pro Diffractometer, Cu Kα). The analysis of the patterns was performed by Rietveld profile refinement using the Fullprof and WinPlotr softwares [19,20].

The high temperature (from 300 K to 600 K) magnetic measurements were carried out using a MANICS DSM8 magneto-susceptometer in an applied magnetic field of 0.05 T. The low temperature (from 5 K to 350 K) field-cooled (FC) measurements were performed using a PPMS apparatus (Quantum Design) in an applied magnetic field of 0.05 T. This device was also used to perform magnetization measurements at 5 K (in fields up to 9 T) and to determine the magnetocaloric properties. The magnetic entropy change ($-\Delta S_M$, given in units of mJ cm^{-3} K^{-1} as suggested by Gschneidner Jr. *et al.* [2]) was evaluated using one of the Maxwell relations:

$$\Delta S_M(T)_{\Delta H} = \mu_0 \int_0^{H_f} \left(\frac{\partial M}{\partial T}\right)_H dH \qquad (1)$$

The numerical integration of Eq. (1) was carried out using the method proposed by Pecharsky and Gschneidner Jr. [21], from magnetization isotherms recorded on heating from 10 K to 350 K in fields up to $\mu_0 H_f = 5$ T, with field steps of 0.2 T and temperature increments of 5 K.

3. Experimental results and interpretation

3.1. Crystallographic data

The analysis of the powder X-ray diffraction patterns, shown in Fig. 1, indicates that $Gd_6(Mn_{1-x}Co_x)_{23}$ compounds (with $x \leq 0.4$) crystallize in the Th_6Mn_{23}-type structure (space group *Fm-3m*) [14] and form a continuous solid solution. The samples are found to be single-phase except for the x = 0.4 alloy, which evidences low intensity supplementary diffraction peaks, corresponding to $Gd(Mn_{1-x}Co_x)_{12}$ and $Gd(Mn_{1-x}Co_x)_2$ phases (Fig. 1). These secondary phases are confirmed on higher cobalt content samples. Rietveld refinement of the $Gd_6(Mn_{0.6}Co_{0.4})_{23}$ pattern indicates less than 4 wt.% of these secondary phases in the sample.

Microprobe measurements indicate that the samples are homogenous, despite lack of annealing, and point to a slight sub-stoichiometry of cobalt (< 2 wt.%) compared to the nominal as weighted compositions. However, this weak sub-stoichiometry is reasonable taking into account the measurement errors. Chemical analysis indicate a maximum Co to Mn substitution of 35(2) at.% in Gd_6Mn_{23}. It is well-known that the limit of solubility commonly decreases with temperature. Then, this experimental value must be considered as a maximum and should not be higher in annealed samples.

Thus, we can conclude that the solubility of cobalt in as-cast $Gd_6(Mn_{1-x}Co_x)_{23}$ is limited to x_{max} ~ 0.35 (±0.02). Considering that secondary phases detected in the x = 0.4 alloy could evidence magnetic properties [22,23], magnetic and magnetocaloric properties of this sample are not taken into account in the study.

The cell parameters and the crystallographic densities of $Gd_6(Mn_{1-x}Co_x)_{23}$ compounds (with $x \leq 0.3$) are gathered in Table 1. As expected from the atomic radii and atomic weights of the involved elements, the Co to Mn substitution leads to a linear decrease of the cell parameter (Fig. 2) and, consequently, to a linear increase of the density. Because of the close X-ray scattering lengths factors of Mn and Co, no attempt has been done to determine the distribution of Co atoms over the four possible transition metal

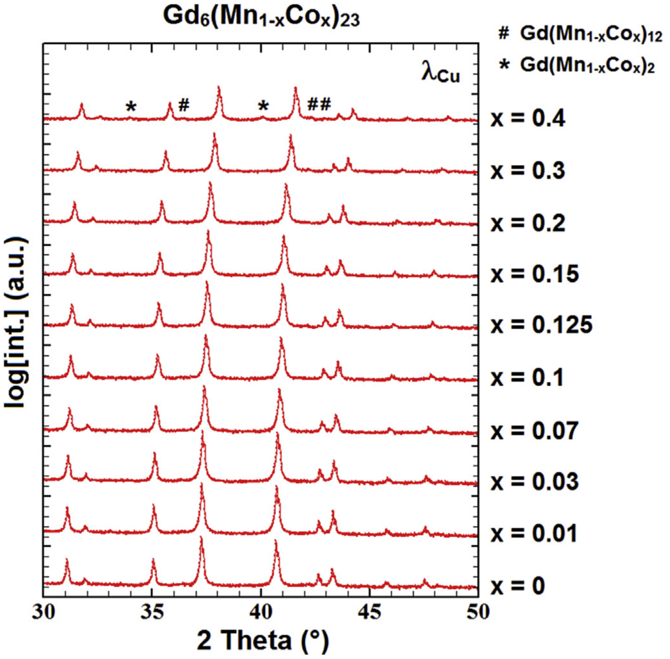

Fig. 1. X-ray powder diffraction patterns at room temperature of $Gd_6(Mn_{1-x}Co_x)_{23}$ ($x \leq 0.4$) represented in logarithmic ordinate scale.