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Effect of stacking blocks on the low field magnetic refrigeration in nanocrystalline Pr_2Co_7 compound

R. Fersi[a], W. Bouzidi[a,b], N. Mliki[a], L. Bessais[b,*]

[a] Université de Tunis El Manar, Faculté des Sciences de Tunis, Laboratoire Matériaux Organisation et Propriétés (LR99ES17), 2092, Tunis, Tunisia
[b] Université Paris Est, ICMPE, UMR7182, CNRS-UPEC, F-94320, Thiais, France

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ABSTRACT

In the present work, we report on magnetocaloric properties of nanocrystalline Pr_2Co_7 compounds in its two polymorphic forms. Magnetic measurements show a second order magnetic transition around T_C of 580 K and 600 K for, respectively for hexagonal (2:7H) and rhombohedral (2:7 R) structures. At a magnetic field change of 1.6 T, the magnetic entropy change $-\triangle S_M^{max}$ = 3.7 J/kg.K for 2:7 R structure, which is much more higher than 2:7H one ($-\Delta S_M^{max}$ = 1.1 J/kg.K). Furthermore, these results show that the magnetocaloric effect is sensitive to the stack configuration. The temperature dependence of the magnetization (M vs. T) and the Arott plots around the second order magnetic transition for this compound are reported. The relative cooling power (RCP) is around 103 J/kg and 8.5 J/kg for 2:7 R and 2:7H structure, respectively. Based on these results, we conclude that Pr_2Co_7 compound with rhombohedral structure (2:7 R) has potential to be magnetic refrigerant for use at low field.

1. Introduction

The nanocrystalline based on rare earth (R) and transition metals (T) are new materials which provide great opportunities for researchers to develop many important technological applications such as permanent magnet and magnetic recording [1–3]. The interest in research on nanocrystalline (R-T) intermetallic compound has increased considerably since it was found that they are suitable materials for magnetic refrigeration over a large temperature span. The magnetic refrigeration is based on the magnetocaloric effect (MCE), it is a green alternative and theoretically more effective that classical cooling systems using cycles of expansion/compression of harmful gases for the environment [4–7]. Unfortunately, the best materials currently used in magnetic refrigeration prototypes are quite limited and still very expensive [8]. The discovery of the MCE in 1997 near the room temperature caused a significant increase of the number of publications in the domain. The search for the ideal material was launched. Many works have been concentrated in finding new magnetic refrigeration materials with excellent performance in a low temperature range and especially those exhibiting second order magnetic transitions. The main characteristics sought are a great magnetocaloric effect and a high refrigerating capacity. Among the families of materials studied for their magnetocaloric effect, we find: Gadolinium (Gd), MNi_x (M = Gd, Sm, Tb, Dy …), manganites: $Mn(As_{1-x}Sb_x)$, $MnFe(P_{1-x}As_x)$, $La(Fe_{13-x}Si_x)$ and Ni_{-55} $Mñ_{-20}Ga_{25}$ [7,9]. The heavy rare earth metal Gd is considered to be the typical working substance for room temperature magnetic refrigeration [10]. A maximum magnetic entropy change ($-\triangle S_M^{max}$) of 10.2 J/kg.K was obtained at 294 K under an applied field change from 0 to 5 T [11].

Recently, research has focused on the R-T intermetallic compounds, especially R-Co intermetallic compounds. R-Co compounds such as R_2Co_{17} [12–14], RCo. [15–18]. and RCo_5 [19] alloys have been studied extensively. However, few quantitative information on the magnetocaloric effect of the R_2Co_7 compounds with the light rare earths has been reported. Ilyn and *al* [20]. have studied the effect in single crystal Nd_2Co_7. The MCE was found to be rather low, $-\Delta S_M^{max}$ = 0.5 J/(kg.K) at 235 K under a field change of 1 T. This makes Nd_2Co_7 inappropriate for utilization in the current magnetic refrigeration applications. Chun and *al* [11]. reported the impact of Ce addition on the magnetocaloric effects of La_2Co_7 compound. For an applied field change from 0 to 50 kOe, the maximum ($-\triangle S_M^{max}$) for $(La_{0.5}Ce_{0.5})_2Co_7$ and $(Ce_{0.65}Pr_{0.35})_2Co_7$ compounds are 0.52 and 0.67 J/kg.K, respectively. But the magnetocaloric properties of the two compounds La_2Co_7 and Pr_2Co_7 have not been studied in detail.

The nanocrystalline Pr_2Co_7 compounds have attracted interest due to their applications as permanent magnets. They exhibit interesting magnetic properties such as large magnetocrystalline anisotropy H_A, and relatively high saturation magnetization M_S. Furthermore, Pr_2Co_7 exhibits a high coercivity H_c of about 18 kOe at 293 K and 23 kOe at 10 K. Also Pr_2Co_7 intermetallics present high Curie temperatures

* Corresponding author.
E-mail address: bessais@icmpe.cnrs.fr (L. Bessais).

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whatever its polymorphic phase. In fact, we have shown [3] that Pr_2Co_7 compound was found to crystallize in two polymorphic forms; a relatively low temperature phase of the hexagonal Ce_2Ni_7 type structure ($P6_3/mmc$ space group), and a high temperature phase of the rhombohedral Gd_2Co_7 type structure ($R\bar{3}m$ space group). It is worthy to note that these phases can be obtained by stacking the hexagonal structural blocks for $PrCo_5$ and the cubic blocks $PrCo_2$ along the common hexagonal axis. The crystalline structural and magnetic properties of the of the Pr_2Co_7 compounds have been published previously [3].

In the present work, we report on magnetocaloric properties for the nanocrystalline Pr_2Co_7 compound. The magnetocaloric effect is calculated in terms of isothermal magnetic entropy change ($-\triangle S_M^{max}$) based on magnetization isotherms obtained at different temperatures from 562 to 598 K and from 582 to 618 K for the rhombohedral (2:7 R) and hexagonal structure (2:7H) respectively. Furthermore, we have discussed the effect of stacking blocks on the low field magnetic refrigeration in nanocrystalline Pr_2Co_7 compound. This study has never been elucidated previously for this type of systems.

2. Experimental details

Pr_2Co_7 alloys were prepared by high-energy ball milling [23,48]. After milling for 5 h with ball to powder ratio of 15/1, under high purity Ar atmosphere, the samples, wrapped in tantalum foil, were annealed for 30 min in sealed silica tube under 10^{-6} Torr at different annealing temperatures T_a = 1000 K and 1350 K [49,50]. The phase constitution and crystal structure were detected by X-ray diffraction (XRD) with CuK_α radiation. Pattern refinements were performed with the FULLPROF computing code based on the Rietveld technique, in the assumption of Thompson-Cox-Hastings line profile [24–26]. The grain size ϕ_{XRD} of the nanocrystalline samples were measured from XRD line broadening analysis applying Scherrer's formula [21,27]. Morphologies, crystal sizes and chemical compositions of the $2Co_7$ alloys were determined by TEM, coupled with EDS, using a JEOL 2010 FEG microscope operating at 200 kV. Specimens for TEM were thinned using a focused ion beam (FIB) type FEI Helios 600 Nanolab dual beam. The magnetic and magnetocaloric properties were determined using differential magnetometer DSM-8 MANICS with field up to 1.6 T.

3. Results and discussion

3.1. Structural properties

Fig. 1 presents, the Rietveld analysis result of XRD patterns of Pr_2Co_7 samples annealed at T_a = 1000 K and 1350 K. The structure refinement performed for the sample annealed at 1000 K shows the presence of a main phase with the hexagonal of the Ce_2Ni_7-type structure ($P6_3/mmc$ space group (No.194)). The lattice parameters are a = b = 5.068 Å and c = 24.463 Å. Pr atoms occupy two crystallographic 4f sites while cobalt atoms occupy 12 k, 6 h, 4f, 4e, and 2a sites. For the sample annealed at 1350 K, the refinement shows the presence of a main phase with the rhombohedral of the Gd_2Co_7-type structure ($R\bar{3}m$ space group (No.166)). The lattice parameters are a = b = 5.068 Å and c = 36.549 Å. In this structure Pr atoms occupy two crystallographic 6c sites while the cobalt atoms occupy 18 h, 9e, 6c, 6c, and 3 b sites. However, we note minor quantities of the oxide phases appearing due to selective oxidation of Pr (Pr_2O_3). The lattice parameters, the atomic positions, R_B and χ^2 factors from Rietveld fit are given in Table 1. Otherwise, 7 structure can be described as a stacking of the hexagonal structural blocks for $PrCo_5$ (structure of the $CaCu_5$ type) and the cubic $PrCo_2$ blocks (structure of the $MgCu_2$ and $MgZn_2$ types) type along the common hexagonal (trigonal for $PrCo_2$) axis. The lattice parameters of the two structures differ by the parameter c, which is larger for the rhombohedral structure due to the difference in stacking ([2H] = [BBA_1BBA_2], [$3R_h$] = 3[BBA_1]) [21,22].

Table 1
a and *c* cell parameters, R_B and χ^2 factors from Rietveld fit for Pr_2Co_7 annealed at T_a = 1000 K and 1350 K.

T_a	1000 K	1350 K
2:7	H	R
Space group	$P6_3/mmc$	$R\bar{3}m$
a (Å)	5.068 (2)	5.068 (3)
c (Å)	24.463 (3)	36.549 (2)
c/a	4.826	7.211
V(Å)	528.63	813.16
χ^2	2.05	3.38
R_B	2.81	4.02

Fig. 2 (a) and (b) show the morphology of the Pr_2Co_7 compound annealed at 1000 K and 1350 K, respectively. The estimated grain size ϕ values are given in the respective figures. The phase was identified as the Pr-Co phase with a stoichiometry 2:7 and can be indexed as a hexagonal (2:7H) structure for Fig. 2 (a) and rhombohedral (2:7 R) one for Fig. 2 (b), which agrees the XRD analysis. The diffraction spots are distributed over the rings corresponding to the distances d_{hkl}: $d_{1\,0\,7}$(0.795 nm), $d_{1\,1\,0}$(0.635 nm), $d_{2\,0\,1}$(0.508 nm), $d_{1\,1\,6}$(0.458 nm), $d_{0\,0\,12}$(0.291 nm), $d_{1\,1\,10}$ (0.258 nm), $d_{2\,1\,7}$(0.158 nm) and $d_{1\,0\,10}$(0.491), $d_{0\,0\,1}$(0.391), $d_{1\,1\,21}$(0.193), $d_{0\,0\,18}$(0.151), for (2:7H) and (2:7 R) structure. The composition of the chemical elements (% at. Co, Pr) was analyzed using the EDS measurement shown in Fig. 2 (c).

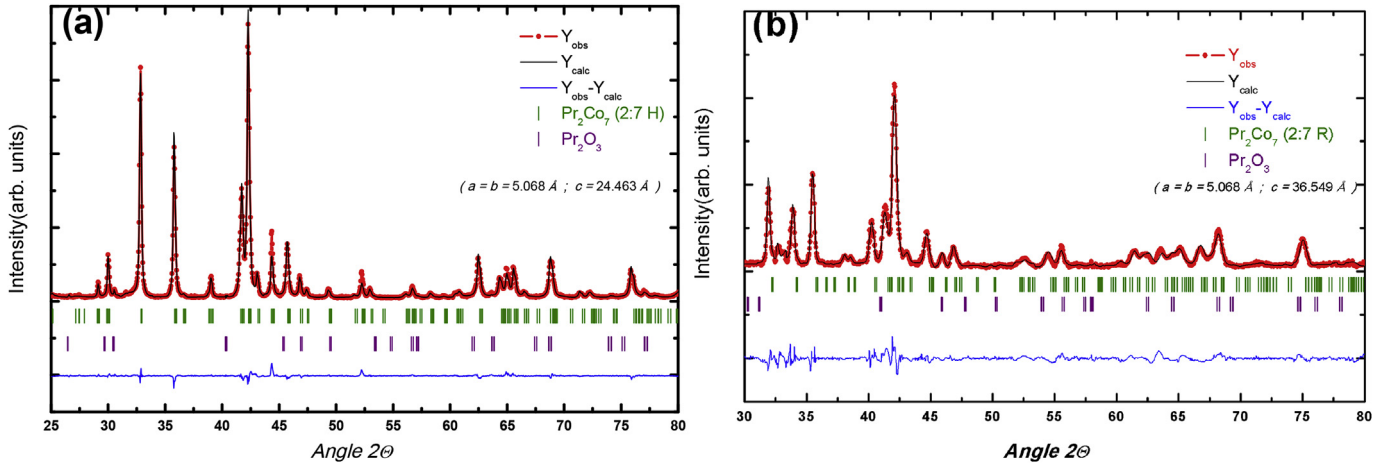

Fig. 1. Rietveld analysis for X-ray diffraction patterns of Pr_2Co_7 compounds annealed at 1000 K (a) and 1350 K (b).