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Research articles

Effect of carbonation on the structural, magnetic and magnetocaloric properties of uniaxial nanocrystalline $Pr_5Co_{19}C_x$ compound

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A B S T R A C T

In this work, we have investigated a multi-scale study of Pr_5Co_{19} carbides. The nanocrystalline $Pr_5Co_{19}C_x$ ($x = 0, 0.5, 1, 1.5$) samples were prepared using two-step method: mechanical milling process and subsequent annealing at 775 °C, followed by a solid-solid reaction carbonation at 420 °C. The structural properties of $Pr_5Co_{19}C_x$ carbides were characterized by X-ray diffraction and refinement Rietveld method. This analysis has revealed that, all samples crystallize in the rhombohedral (3R) of Ce_5Co_{19}-type structure (space group $R\bar{3}m$). The lattice parameters have increased with carbon content. Due to the magnetovolume effect, the Curie temperature was enhanced by about $\frac{\Delta T_C}{T_C} = 10\%$. The coercivity H_c of these carbides have decreased versus x. In addition, the magnetocaloric effect (MCE) have been studied by isothermal magnetization measurements. The low field entropy change ($|\Delta S_M^{max}|$) present a maximum of 5.2 J/kg.K for $x = 0$ and decreases when C content is increasing. The Arott plots and temperature dependence of the magnetization around second order magnetic transition are reported.

1. Introduction

Intermetallics that contain rare earth (R) elements [1–3] are particularly interesting because they give rise to a great variety of functional materials for technological applications[4].

They are of interest also in understanding fundamental physics and metallurgical properties. In fact, the intemetallics compounds present three intrinsic properties, that are of critical importance for applications such as permanent magnets: high Curie temperature T_C, significant saturation magnetization M_S and high uniaxial anisotropy, which is conventionally represented by an anisotropy field H_a.

It is also important to note that, R-T compounds (R: rare earth, T: Transition metal) offer a good magnetic refrigeration properties. This silent cooling technique due to the absence of compressor which leads to an energy saving technology [5,6].

The insertion of a light element such as N, H and C is very interesting for many technology applications [7,8]. It results to an increase of the lattice parameters and then the unit cell volume with insertion. The effect of the light element in the crystallographic cell, also is observed by an improvement of intrinsic magnetic properties (T_C, M_S, magnetocrystalline anisotropy, …) of $PrTi(Fe,Co)_{11}C$ [9], $Sm(Fe,Si)_9C$ [10], $Sm(Fe,Ga)_9C$ [11] compounds.

Among these systems, the transition metal rich Pr_5Co_{19} intermetallics have attracted considerable attention, due to their significant intrinsic and extrinsic magnetic properties.

In this work, the nanocrystalline Pr_5Co_{19} carbides have been synthesized and characterized for the first time. We are interested in the influence of the carbonation on the nanocrystalline Pr_5Co_{19}. We present the result of structural studies performed by X-ray diffraction using the Rietveld method for $Pr_5Co_{19}C_x$ nanostructured materials. Carbon was chosen for its stability compared to the hydrides. The variation of the Curie temperature and the influence of C insertion ($x = 0, 0.5, 1, 1.5$) on the extrinsic magnetic properties have been studied. Also, the low field magnetocaloric effect has been thoroughly reported.

2. Experiment

The Pr_5Co_{19} carbides were prepared by arc melting in a water-cooling cooper hearth with an unconsumable tungsten electrode under purified argon atmosphere. An excess of praseodymium was used in order to maintain an over pressure of Pr on the sample. Milling was performed for 5 h with ball to powder of 15/1 in a high-energy ball milling [12,13]. After the synthesis, the powder was wrapped into tantalum fail, annealed for 30 min is sealed silica tube under 10^{-6} Torr at 775 °C, in order to prevent oxidation under heating, and followed by quenching in water. This technique is well adapted to volatile elements with a good control of stoichiometry.

To insert the carbon in the unit cell, we have used a solid–solid reaction. The technique is based on reacting the Pr_5Co_{19} powder with anthracene ($C_{14}H_{10}$). In the same time, pieces of magnesium, separated by silica wool, are placed in the ampoule. This is followed by an annealing in silica ampoule sealed under high vacuum at 420 °C for 24 h.

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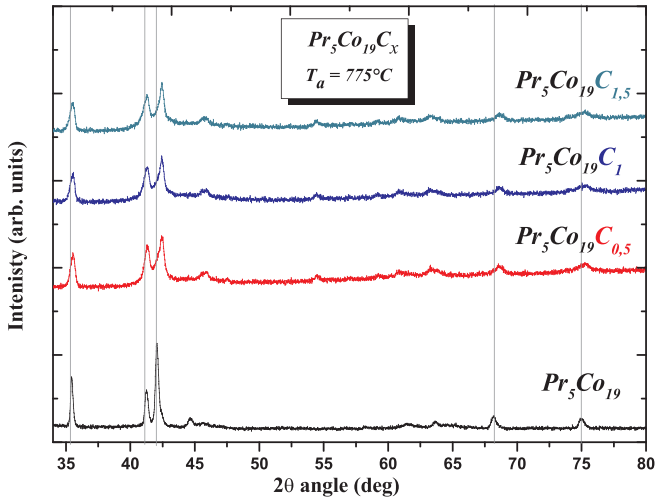

Fig. 1. XRD patterns of nanocrystalline $Pr_5Co_{19}C_x$ (x = 0, 0.5, 1, 1.5) compounds, annealed at 775 °C.

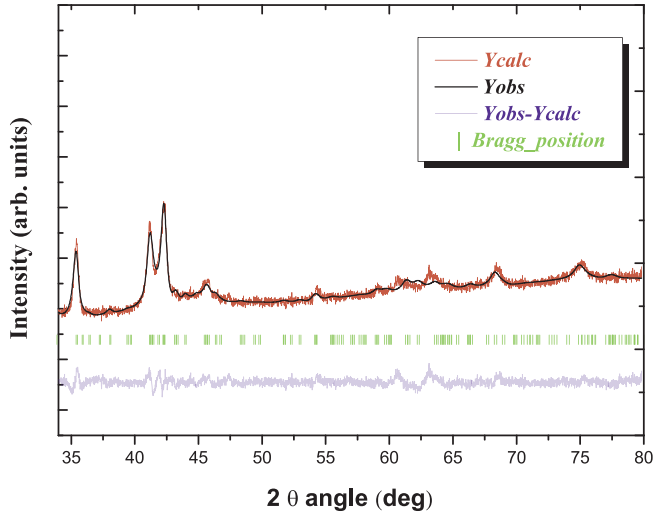

Fig. 2. Rietveld analysis for X-ray diffraction pattern of $Pr_5Co_{19}C_{0.5}$ compound annealed at 775 °C.

The anthracene decomposes releasing hydrogen gas, which is trapped by the pieces of magnesium. The solid–solid reaction involves that C atoms diffuse and release into the compound according to the following equation:

$$7Pr_5Co_{19} + \frac{1}{2}C_{14}H_{10} + \frac{5}{2}Mg \Rightarrow 7(Pr_5Co_{19})C + \frac{5}{2}MgH_2$$

The phase analysis was studied using powder X-ray diffraction (XRD) on a Bruker D8 diffractometer. The used wavelength is the average wavelength of $K_\alpha 1$ and $K_\alpha 2$ with data collected by 0.015° step width for 13.5 s, and analysed by Rietveld method [14–17]. The line shape of the diffraction peaks was generated by a pseudo-Voigt function. The background was shown by interpolation between selected points in regions devoid of Bragg reflections. In the final run the following parameters were refined: zero point, scale factor U, V, W, unit cell parameters, background points, positional parameters, isotopic thermal factors and preferred orientations parameters. The "goodness-of-fit" indicators R_B and χ^2 are calculated as follows [18,19,12]:

$$R_B = \frac{\sum_K |I_K(o) - I_K(c)|}{\sum_K I_K(o)}$$

and

$$\chi^2 = \frac{\sum_i w_i |y_i(o) - y_i(c)|^2}{N - P + C}$$

$I_K(o)$ is the observed Bragg intensity and $I_K(c)$ is the calculated one. N is the number of measured points in the diagram, P the number of refined parameters and C the number of constraints.

Measurements of the intrinsic magnetic (T_C) and magnetocaloric properties ($|\Delta S_M|$) were carried out using differential sample magnetometer MANICS in a field of 1 kOe and heating rate of 5 K/min with around 5–10 mg sample. T_C has been determined by the maximum of the absolute value of the first-order derivative of the magnetization with respect to temperature [20,21]. Extrinsic magnetic measurements were performed using a physical property measurement system (PPMS) Quantum Design, at 293 K with field up to 90 kOe.

3. Results and discussion

3.1. Structure analysis

Fig. 1 shows XRD patterns of $Pr_5Co_{19}C_x$ (x = 0, 0.5, 1, 1.5). We can see that the diffraction peaks are shifted reflecting the increase of lattice parameter, as a result the unit cell volume V increases with C atoms content. It's important to note that whatever the annealing temperature, the system crystallizes in the rhombohedral (3R) of Ce_5Co_{19}-type structure [22].

Additionally, Pr_5Co_{19} structure can be described by stacking the hexagonal structure blocks of $PrCo_5$ ($CaCu_5$-type structure) and the cubic blocks of $PrCo_2$ ($MgCu_2$-type structure) along the c-axis. Previous study of nanocrystalline Pr_5Co_{19} [22] has shown that Pr atoms occupy two inequivalent crystallographic sites 6*c* and 3*a*, while cobalt atoms occupy three crystallographic sites 6*c*, 18*h* and 3*b*, the lattice parameter were $a = b = 5.0672(4)$ Åand $c = 48.755(4)$ Å.

Rietveld refinement for the $Pr_5Co_{19}C_{0.5}$ (Fig. 2) shows that the carbides conserve always the rhombohedral structure for alloy annealed at 420 °C for 24 h. As a result, the crystallographic sites which can receive C are 9*e* and 36*i*, with a good result of specific factors values: χ^2 and R_B. Carbon atoms crystallographic sites of $Pr_5Co_{19}C_x$ are presented in Fig. 3.

With increasing C content, the unit cell parameters are affected, their relative variation are $\frac{\Delta a}{a}$ = 0.27% and $\frac{\Delta c}{c}$ = 1.57% (Fig. 4). The unit cell volume V expansion $\frac{\Delta V}{V} = \frac{V_C - V}{V}$ varies from 0.42% for x = 0.5–0.7% for x = 1.5. V_C and V are the volume of carbonated cell and that of the non carbonated one, respectively. The values of the structural parameters are given in Table 1 as a function of x content.

Compared with the nanocrystalline $Pr_2Co_7C_x$ [23], the same phenomenon is observed, the insertion of carbon leads to an increase of the lattice parameters: $\frac{\Delta a}{a}$ = 0.23%, $\frac{\Delta c}{c}$ = 10.5% and $\frac{\Delta V}{V}$ = 10% for x = 1.

3.2. Magnetic properties

The Curie temperature, also called the magnetic ordering temperature, is a direct measure of exchange interaction which is the origin of ferromagnetism. It's known that in rare earth transition metal intermetallic, T_C is governed by three kinds of exchange interactions: the 3*d*–3*d* exchange interaction (J_{Co-Co}) between the magnetic moments of the Co sublattice, 4*f*–4*f* exchange interaction (J_{R-R}) between the