STUDIA UBB PHYSICA, Vol. 63 (LXIII), 1-2, 2018, pp. 9-18
(RECOMMENDED CITATION)
doi:10.24193/subbphys.2018.01

MAGNETOCALORIC EFFECT AND MAGNETIC PROPERTIES OF $Pr_{1-X}Ce_XCo_3$ COMPOUNDS

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ABSTRACT. Magnetic properties and magnetocaloric effect under moderate magnetic field in polycrystalline $Pr_{1-x}Ce_xCo_3$ compounds with $x = 0$, 0.1, 0.2, 0.3, and 0.4 are reported. The powder X-ray diffraction measurements show that all samples crystallize in the rhombohedral $PuNi_3$-type structure (space group: R-*3m*), specific for $PrCo_3$, with the lattice parameters decreasing with the cerium content. The magnetic measurements indicate a transition from a magnetic order state to a paramagnetic one below room temperature. The Curie temperature decreases roughly linear with the Ce concentration from 270 K for $x = 0.1$ to 146 K for $x = 0.4$. A moderate magnetocaloric effect was found for all samples, with the maximum entropy change located at temperatures near the magnetic transition ones.

Keywords: *rare earth based intermetallic compounds, Curie temperature, magnetocaloric effect.*

1. INTRODUCTION

The magnetic properties and magnetocaloric effect investigations of *R -T* (*R* = rare earth,*T* = transition metal) intermetallic compounds has been the subject of many theoretical and experimental studies, due to their potential technological applications as magnetic refrigerating materials around room temperature.

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Magnetocaloric effect is an intrinsic phenomenon for magnetic materials and can be defined as the absorption or emission of heat when a magnetic material is subjected to a change of a magnetic field [1-2]. Closely related to the MCE value and to magnetic contribution to the heat capacity is magnetic entropy and its change. The magnetic entropy change (ΔS_m) is also a tool used to determine the capacity of the magnetic refrigerators. *R-T* based intermetallic systems have been intensively investigated and reported to have large MCE in a wide temperature range, depending on the constituent elements and composition [3-5].

Among these series of compounds, *R*-Co_3 intermetallic compounds have attracted a lot of scientific interest due to their wide applications as permanent magnets and due to their excellent magnetic properties, such as large magnetocrystalline anisotropy and important saturation magnetization at room temperature [6].

R-Co_3 compounds crystalize in the rhombohedral $PuNi_3$-type structure (space group: R-*3m*). The unit cell contains two crystallographic sites for R atoms (3a and 6c) and three crystallographic sites for Co atoms (3b, 6c and 18h) [7] The important magnetic properties of RCo_3 are the result of the combination of *4f* - localized and *3d* - itinerant magnetism [8] Usually, the transition metal, Co is the one which provides high transition temperature and saturation magnetization, while rare earth element, *R* provides high magnetocrystalline anisotropy.

Previously, $PrCo_3$ was reported to be highly anisotropic uniaxial ferromagnet [9-11] with the easy magnetization direction parallel to the c-axis and the Curie temperature of 349 K [6]. Unlike other RCo_3 compounds, $CeCo_3$ shows different magnetic behavior like very low transition temperature (~50 K) and a low value of magnetic susceptibility. The *3d* weak magnetism in $CeCo_3$ compared with other members of RCo_3 compounds indicate that Ce is probably in an intermediate valence state [12-14]. Previous studies of magnetocaloric effect on *R*-Co_3 compounds with Al substitution on Co site [15] show that hybridization effects cause the adjustment of the transition temperature through the room temperature. Depending on the dopant concentration, a significant value of the magnetic entropy changes around transition temperature can be obtain. The experimental reports suggest that these types of compounds can be used for magnetic refrigeration.

This paper reports on the elaboration of polycrystalline samples of $Pr_{1-x}Ce_xCo_3$, the structural, magnetic and magnetocaloric properties, not investigated so far, to our best knowledge.

2. EXPERIMENTAL DETAILS

The samples of $Pr_{1-x}Ce_xCo_3$ (x = 0, 0.1, 0.2, 0.3, 0.4) were prepared by arc-melting technique, under highly purified Ar atmosphere from high purity of Pr, Ce and Co (>99.9%) acquired from Alfa Aesar. Several consecutive meltings were performed to ensure homogeneity and a small excess of rare earth element (3% Ce and 1% Pr) was used in order to compensate for losses during melting. The samples were heat treated at 850 ºC in vacuum for 7 days and slowly cooled to room temperature. The crystallographic structure of the samples was checked by X-ray powder diffraction technique, at room temperature using a Bruker D8 Advance AXS diffractometer with Cu Kα radiation. All the magnetic investigations were performed in the temperature range 4 - 300 K and external magnetic field up to 12 T, using a 12 T Vibrating Sample Magnetometer (VSM) from Cryogenics. The magnetic entropy changes were calculated from magnetization isotherms, between zero field and a maximum field (H_0) using the thermodynamic relation:

$$\Delta S_m(T,H_0) = S_m(T,H_0) - S_m(T,0) = \frac{1}{\Delta T}\int_0^{H_0}\left[M(T+\Delta T,H) - M(T,H)\right]dH \qquad (1)$$

with an increment in temperature between measured magnetization isotherms of ΔT = 5K. The refrigerant capacity or the relative cooling power (RCP) was used to evaluate the magnetic refrigeration of materials:

$$RCP(S) = -\Delta S_m(T,H) \times \delta T_{FWHM} \qquad (2)$$

where ΔS_m is the maximum value of the magnetic entropy change and δT_{FWHM} its full-width at half-maximum.

3. RESULTS AND DISCUSSION

The crystal structure of $Pr_{1-x}Ce_xCo_3$ was investigated by powder X-ray diffraction. As shown in **Figure 1**, these compounds crystallize in the rhombohedral $PuNi_3$-type structure (space group: R-*3m*), specific for $PrCo_3$.

The lattice parameters listed in **Table 1** were obtained by Rietveld refinement using Fullprof software [16] on the measured patterns; a representative result is shown in **Figure 2**. The obtained values for lattice parameters are in good agreement with those reported previously for $PrCo_3$ [17]. The Ce doped samples show slightly smaller values for both lattice parameters than those for $PrCo_3$, as expected considering the smaller ionic radius of the cerium compared to the praseodymium ionic radius. **Figure 3** shows the decrease of the lattice parameters on the *a*- axis, almost linearly, as the cerium concentration is increasing. The c lattice parameters remain almost constant.

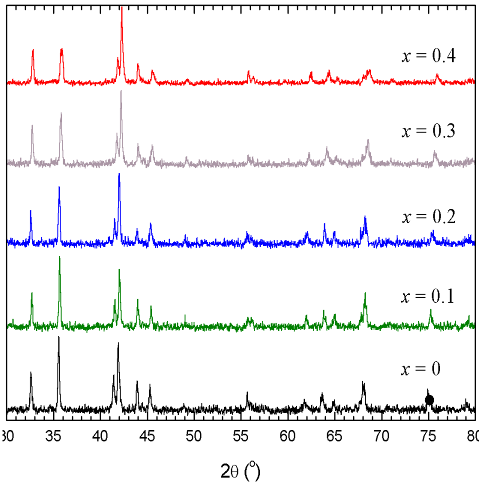

Figure 1. X-ray diffraction patterns for the $Pr_{1-x}Ce_xCo_3$ samples

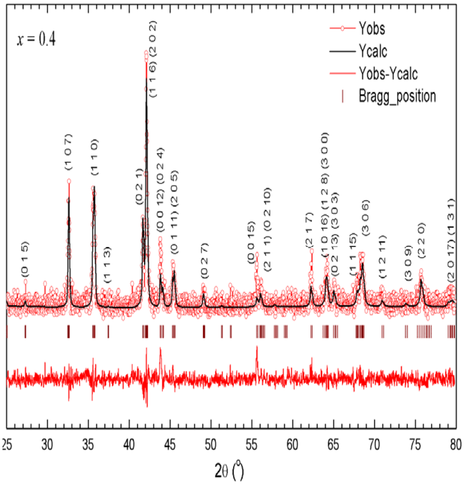

Figure 2. X-ray diffraction pattern together with the calculated profile using Rietveld method and difference curve of the $Pr_{0.6}Ce_{0.4}Co_3$ sample

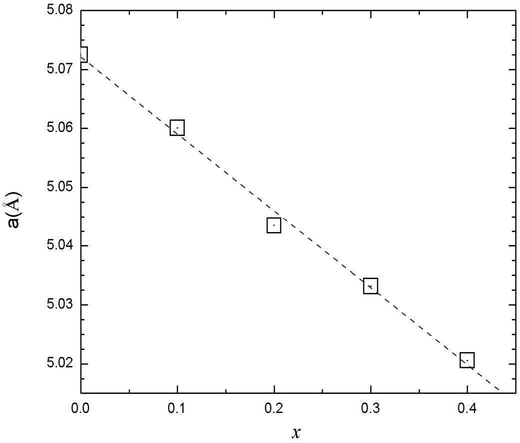

Figure 3. The concentration dependence of *a* lattice parameter for $Pr_{1-x}Ce_xCo_3$ samples

Table 1. Refined lattice parameters of$Pr_{1-x}Ce_xCo_3$ investigated samples

x	a(Å)	c(Å)
0	5.07(2)	24.81(1)
0.1	5.06(1)	24.79(7)
0.2	5.04(4)	24.77(4)
0.3	5.03(3)	24.78(1)
0.4	5.02(1)	24.77(7)

Zero Field Cooled (ZFC) – Field Cooled (FC) magnetization measurements were performed under a moderate applied magnetic field of 0.05T, in the temperature range of 4 – 300 K as plotted in **Figure 4,** for the samples with x = 0.1 and x =0.2. Both ZFC and FC curves show a typical paramagnetic to ferromagnetic transition. The difference between the ZFC and FC curves below the ordering temperature increases with Ce content. The spin-glass like features [18-19], may be due to the presence of a possible magnetic disorder and the magnetocrystalline anisotropies [20].

The transition temperatures from the paramagnetic state to the magnetic order one defined as the temperature corresponding to the minimum of $\delta M / \delta T$ were calculated and plotted for all samples, as shown

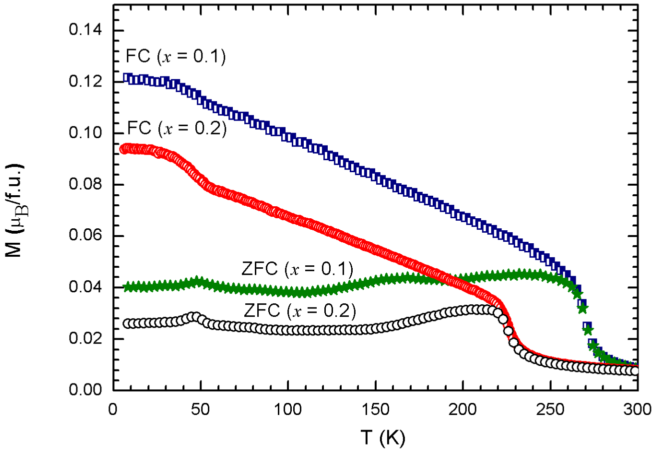

Figure 4. Temperature dependences of magnetization measured in zero field-cooling (ZFC) and field-cooling (FC) modes for all samples

in **Figure 5.** A decrease, almost linearly, of the transition temperature is observed with the increase of the Ce concentration, from 270 K for $x = 0.1$ to 146 K for $x = 0.4$. The reduction of the magnetic ordering temperature is caused by the changes associated with hybridization of 5*d* orbitals of Ce and 3*d* orbitals of Co and the intersublattice 3*d*-4*f* exchange interaction (J_{PrCo}) which decreases with the substitution of Pr for Ce [21].

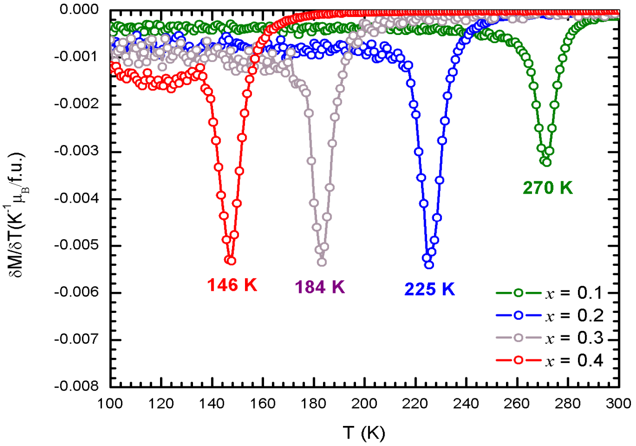

Figure 5. The first derivative of the magnetization versus temperature and the transition temperature for all samples

The magnetization isotherms measured between T = 100 K and T = 300 K are shown in **Figure 6**, for the sample with *x* = 0.2. The measurements indicate the same trend for all samples, the saturation being not reached until the 12 T value of the applied magnetic field. The difficulty of approaching a magnetic saturation state can be explained by the spin glass like behavior also highlighted by ZFC-FC measurements.

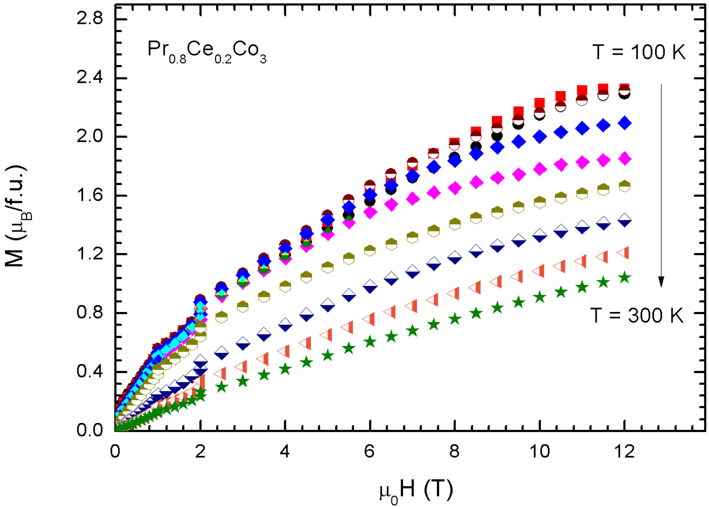

Figure 6. Magnetization isotherms for $Pr_{0.8}Ce_{0.2}Co_3$ in the temperature range 100 K and 300 K

The Arrot plots for $Pr_{0.8}Ce_{0.2}Co_3$, calculated from the magnetization isotherms around the transition temperature are represented in **Figure 7**. The Arrot curves for all samples display a second order magnetic phase transition from a ferromagnetic to a paramagnetic state at T_c, a specific feature for magnetic refrigerants.

The magnetic entropy changes were calculated based on the magnetization isotherms measured between 200 K and 300 K, with a step of 5 K, in the external magnetic field of 2 T and 4 T and plotted as a function of temperature in **Figure 8.** The maximum value of the magnetic entropy change is reached at temperatures close to the magnetic transition ones, for all the investigated samples. The substitution of Ce for Pr causes a decrease in maximum entropy change values, as listed in **Table 2**. This decrease in maximum values of magnetic entropy change may be caused by the decrease in the concentration of the Pr ions and by the disorder. Nevertheless, the $|\Delta S_m|$ peaks are broader, which is mandatory for a good refrigerant material. Moreover, it can be observed that the curves are nearly symmetric distributed around the transition temperature, a behavior generally characteristic for materials exhibiting a second order magnetic phase transition [22].

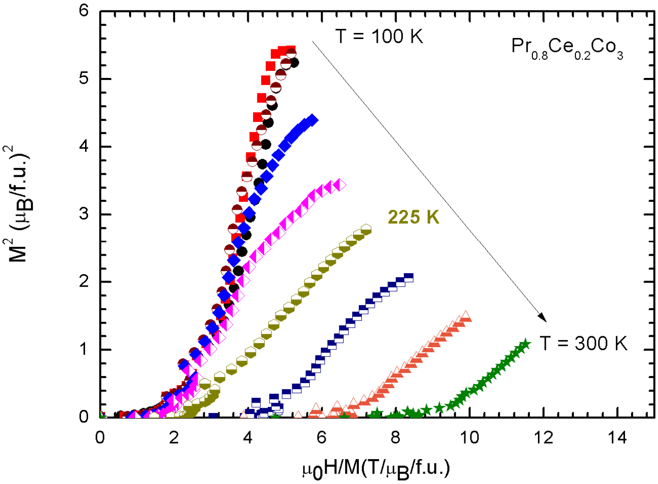

Figure 7. Arrot plots for $Pr_{0.8}Ce_{0.2}Co_3$ sample.

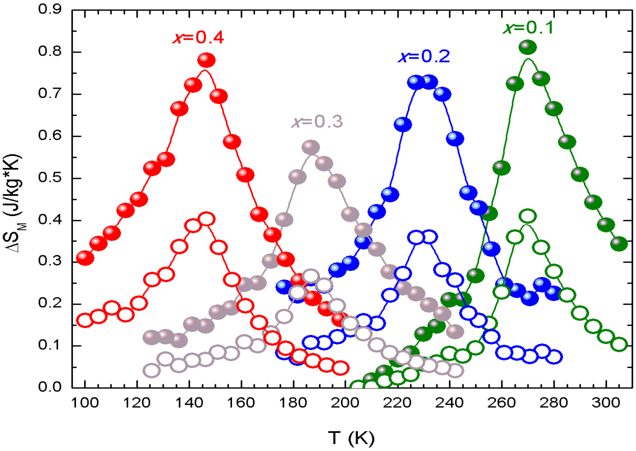

Figure 8. The temperature dependences of the magnetic entropy change for $Pr_{1-x}Ce_xCo_3$ compounds in ΔH=4T and ΔH=2T

The magnetic refrigeration efficiency was evaluated by calculating the relative cooling power (*RCP*) for all the investigated samples. The RCP*(S)* values, presented in **Table 2**, indicate that the materials could be used for the magnetic refrigeration applications.

Table 2. Magnetocaloric properties of $Pr_{1-x}Ce_xCo_3$ compounds

x	T_{max} (K)	$\lvert\Delta S_M\rvert$ (J/KgK)		δT_{FWHM} (K)		RCP(*S*) (J/kg)	
		ΔH=4T	ΔH=2T	ΔH=4T	ΔH=2T	ΔH=4T	ΔH=2T
0.1	270	0.81	0.41	44	30	35.6	12.3
0.2	230	0.72	0.36	46	34	33.1	12.2
0.3	188	0.55	0.27	48	35	26.4	9.45
0.4	146	0.78	0.40	60	41	46.8	16.4

CONCLUSIONS

The structural, magnetic and magnetocaloric properties of $Pr_{1-x}Ce_xCo_3$ have been studied. All samples crystallize in the rhombohedral $PuNi_3$-type structure, with the lattice parameters slightly smaller than those for $PrCo_3$. The magnetic measurements indicate a roughly linear decrease of the transition temperature with Ce concentration, from 270 K for x = 0.1 to 146 K for x = 0.4. The decrease in Curie temperature could be attributed to the changes associated with hybridization of 5*d* orbitals of Ce and 3*d* orbitals of Co and the intersublattice 3*d*-4*f* exchange interaction (*J*PrCo) which is weaker by substitution of Pr for Ce.

A moderate magnetocaloric effect was found for all samples, with the maximum entropy change located at temperatures near the magnetic transition ones. Allthough the maximum value of the magnetic entropy changes decreases with increasing cerium content, moderate RCP(*S*) values were obtained for all samples due to the large δT_{FWHM} values.

Considering the possibility of choosing the appropriate concentration for constituents, to tune the transition temperature and the magnetocaloric effect, together with the high RCP(*S*) values and the broadened magnetic entropy curves, these materials are promising candidates for magnetic refrigeration devices.

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