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Influence of Substitution and Milling on Structural and Magnetic Properties of Selected $\text{Sm}(\text{Ni}_{1-x}\text{Co}_x)_3$ Compounds

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The influence of substitution of Co for Ni in $\text{Sm}(\text{Ni}_{1-x}\text{Co}_x)_3$, where $x = 0.0, 0.1, 0.2$, on the structural and magnetic properties has been investigated. Samples with $x = 0.0$ and 0.2 were subjected to grinding in a high energy ball mill. The presence of a PuNi_3 type of crystal phase was evidenced for bulk crystalline and powders specimens. With an increase in the cobalt content, an increase at T_c was observed. From the magnetic isotherms, the magnetic entropy changes were determined both for solid and powdered samples. It has been shown that the value of the magnetic entropy change at T_c is doubled for the bulk sample with $x = 0.2$ but it has decreased significantly for all powdered samples.

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1. Introduction

Rare earth and transition metals intermetallic compounds such as alloys were widely studied in previous years because of interesting 3d-4f effects and a possibility of application in different branches of industry and technique [1,2]. Generally, the magnetic properties of rare earth and transition metals depend on crystal structure because the atoms of transition elements have an exposed 3d shell and are susceptible on their nearest surrounding. In recent years, nanocrystalline RE/3d alloys have attracted an increasing interest because of their enhanced magnetic parameters while compared to their bulk counterparts [3,4,5]. As an example, one can mention a high coercivity of 33 kOe for the nanocrystalline SmCo_3 compound. In this paper, we focus on structural and magnetic changes in a SmNi_3 compound upon the Ni/Co substitution and pulverization to a size of approximately 100 nm.

2. Experimental

$\text{Sm}(\text{Ni}_{1-x}\text{Co}_x)_3$ samples where $x = 0.0, 0.1$ and 0.2 were prepared by arc melting of high purity elements (99,99% purity) under argon atmosphere. An excess 5% wt. of Sm element was added to overcome the weight loss during the melting. To obtain a high homogeneity of the prepared compounds, all samples were re-melted several times. Afterwards, the as-cast samples were wrapped in tantalum foil, placed in quartz tubes and annealed at 900 °C for 196 h. Samples of $\text{Sm}(\text{Ni}_{1-x}\text{Co}_x)_3$ with the highest purity were powdered in a high energy ball mill Mixer Mill 400 (Retsch) with a frequency of 30 Hz for 12 h

and 24 h. The grinding procedure, described earlier in [1], was carried out in dimethylformamide (DMF) using Eppendorf vials and 2 mm balls made of ZrO_2 ; the balls to powder ratio was close to 5:1 by weight. The crystal structure was measured by X-Ray Diffraction method on an Empyrean XRD diffractometer (PANalytical). All measurements were carried out at room temperature using a Cu X-ray source. Electron Microscopy (SEM) studies were carried out using Jeol JSM 6480 operated at 20 kV after 24 h of grinding. All examined powders were fixed to the sample holder by the carbon double coated conductive tape. The SEM images were taken in the SE mode in the magnification range of 2000 to 40000 times. All magnetic measurements were performed on a SQUID (superconducting quantum interference device) magnetometer MPMS XL7 (Quantum Design). Temperature measurements were conducted in the range of 2 K to 400 K. The magnetic field was being changed up to 7 T.

3. Results and discussion

3.1. Crystal structure

Crystal structures of all measured samples were refined using the Rietveld method. The match function used to analysis and approximation was a Pseudo-Voigt function with UWV parameters (using the FullProf program). The analysis showed that all the samples crystallized in a PuNi_3 -type of structure ($R\bar{3}m$ space group). For the sample with $x = 0.1$, the diffraction patterns showed a presence of an additional phase SmNi_2 , around 3% by weight of the whole sample. The example XRD pattern of $\text{Sm}(\text{Ni}_{0.8}\text{Co}_{0.2})_3$ is showed in Fig.1. The cell parameters change from $a = 5.0040 \pm 0.0009$ Å and $c = 24.6223 \pm 0.0026$ Å for SmNi_3 to $a = 5.0130 \pm 0.0123$ Å and $c = 24.6648 \pm 0.0151$ Å for $\text{Sm}(\text{Ni}_{0.8}\text{Co}_{0.2})_3$. The character of these changes is linear. This increase in the cell parameters is due to the difference in atomic radii of

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nickel and cobalt. Cobalt has a greater atom radius than nickel, causing an extension of the primitive cell. With the increase of the milling time, a gradual amorphization was observed (Fig. 1).

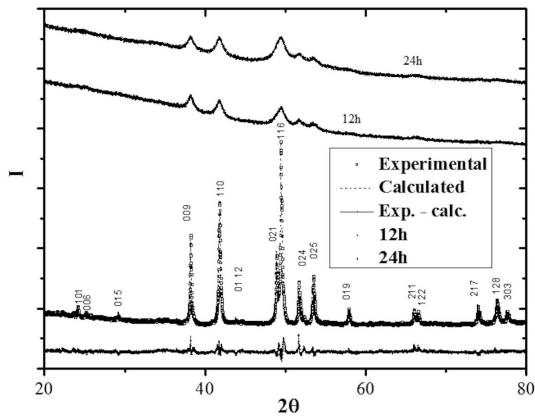


Fig. 1. XRD diffraction patterns for bulk $\text{Sm}(\text{Ni}_{0.8}\text{Co}_{0.2})_3$ and vanishing of the crystal structure of ground $\text{Sm}(\text{Ni}_{0.8}\text{Co}_{0.2})_3$.

The values of the crystallites size determined by the use of the Scherrer's equation [6] are reduced by milling for the two synthesized samples. However, for pure SmNi_3 , this parameter varies from 68.87 ± 3.50 nm (bulk sample) to 20.29 ± 1.40 nm (24 h), whereas for the $x = 0.2$, it is reduced from 45.02 ± 2.30 nm (bulk sample) to 15.80 ± 0.80 nm (24 h), respectively. It is worth mentioning that the value of the obtained crystallites is smaller than that obtained from SEM images, because the crystallites size is not synonymous with the particles size, which is visible on SEM picture (see Fig. 2).

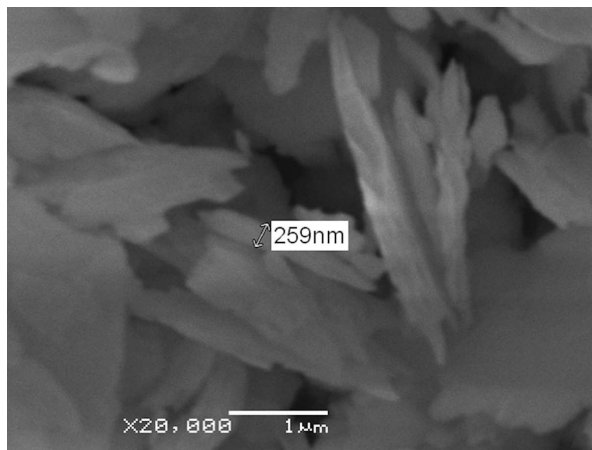


Fig. 2. SEM image obtained for the SmNi_3 compound.

3.2. Magnetic properties

The temperature dependence of magnetization $M(T)$ has been measured at the applied field of 0.1 T. The temperature of phase transition T_c for each sample has been estimated from dM_{FC}/dT as the minimal value. The values of T_c are shown in Fig. 3. It was observed

that an increase in the Co content is accompanied by a rapid increase in the values of T_c and magnetization. The growth of T_c may be caused by changes in magnetic interactions between atoms as a result of doping. Interactions in these compounds are mainly derived from those within the $3d - 3d$ band of nickel/cobalt and $3d - 4f$ band of nickel/cobalt and samarium. The increase in the magnetization with the Ni/Co substitution may be related to the fact that Co has a higher magnetic moment than the Ni atom. In the magnetically ordered state, all compounds exhibit remarkable thermomagnetic irreversibility (Fig. 3). In the field cooled (FC) mode, the $M(T)$ dependence shows an increase at low temperatures until saturation. However, in the zero field cooled (ZFC) mode, the $M(T)$ curves are quite different. In all $M_{ZFC}(T)$ curves, the maxima are visible, after which the values of $M_{ZFC}(T)$ fall to zero at low temperatures. The unusual shape of the ZFC curves as well as the large FC-ZFC difference may be related to a high magnetic anisotropy of these compounds. For SmNi_3 and $\text{Sm}(\text{Ni}_{0.9}\text{Co}_{0.1})_3$, a small negative magnetization $M_{ZFC}(T)$ was observed at low temperatures. It may be caused by the trapped field in a superconducting magnet. This phenomenon and its mechanism are briefly described in Kumar's article [7]. The magnetocaloric effect (MCE) was evaluated using the formula (1), based on a family of magnetic isotherms $M(H)$ measured at different temperatures:

$$\Delta S_M [H_m, T] = \int_0^{H_m} \left(\frac{\partial M}{\partial T} \right)_H dH, \quad (1)$$

where $\Delta S_M[H, T]$ is the magnetic entropy change at a temperature T due to a magnetic field change from 0 to H_m .

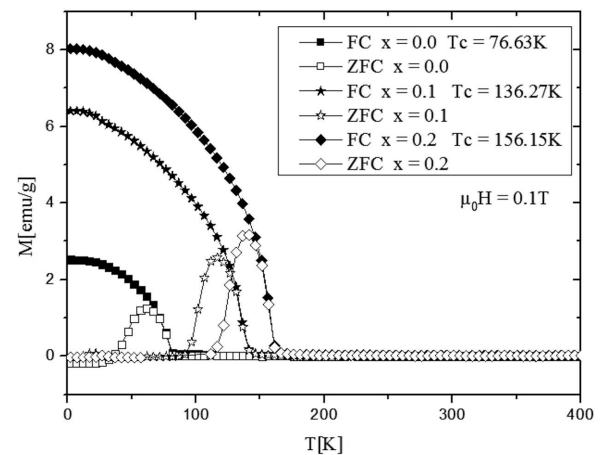


Fig. 3. FC/ZFC magnetization curves of $\text{Sm}(\text{Ni}_{1-x}\text{Co}_x)_3$.

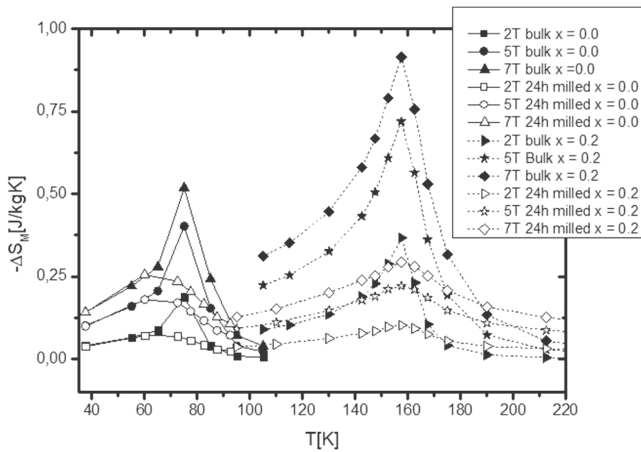
In Fig. 4, the magnetocaloric effect of SmNi_3 and $\text{Sm}(\text{Ni}_{0.8}\text{Co}_{0.2})_3$ is presented for the bulk form as well as after 24 h of grinding. It is observed that the replacement of nickel by cobalt increases the value of the magnetocaloric effect. In the field of 2 T, the value of

magnetic entropy changes from 0.188 J/kgK for SmNi_3 to 0.367 J/kgK for $\text{Sm}(\text{Ni}_{0.8}\text{Co}_{0.2})_3$. Furthermore with the increase of the magnetic field, the values of entropy changes grow linearly. As expected, the maximum value of entropy decreases with progressive time of milling, which is observed in other papers [1, 2, 8]. In SmNi_3 , the position of the MCE maximum changes from 76 K for bulk to 60 K for the milled sample. This effect may be related to the weakening of the interactions between the magnetic particles with grinding. No similar shift for $\text{Sm}(\text{Ni}_{0.8}\text{Co}_{0.2})_3$ was observed. From $M(H)$ curves, the saturation magnetization M_s and the coercivity H_c were obtained. Chemical substitution and milling have a big impact on the values of $M(H)$ and H_c . The coercivity dropped from 5.53 T for SmNi_3 to 0.27 T for $\text{Sm}(\text{Ni}_{0.8}\text{Co}_{0.2})_3$. The saturation $M_s(x)$ also has changed with the replacement of Ni by Co having a greater magnetic moment and it increased from $0.06 \mu_B/\text{fu}$ for $x = 0.0$ to $0.106 \mu_B/\text{fu}$ for $x = 0.2$. The pulverization of the samples caused an extreme decrease in the H_c and an increase in the M_s value.

TABLE I

Values of magnetic parameters of the examined materials.

x	T_c [K]	$-\Delta S_M$ (5 T) [J/kg K]	μ_{eff} [μ_B/fu]	H_c (2 K) [T]	M_s (2 K) [μ_B/fu]
0.0	76	0.188	0.041	5.53	0.060
0.1	136	-	0.061	1.03	0.069
0.2	156	0.367	0.091	0.270	0.106
0.0 (24 h)	60	0.069	-	0.135	0.216
0.2 (24 h)	156	0.102	-	0.130	0.352

Fig. 4. Magnetic entropy changes of bulk and powder $\text{Sm}(\text{Ni}_{1-x}\text{Co}_x)_3$.

Applying the modified Curie-Weiss law to bulk samples in paramagnetic state, the effective magnetic moments μ_{eff} were obtained. An increase in the value of the effective moment μ_{eff} with the increase in the cobalt concentration has been observed. The values were $0.041 \mu_B/\text{fu}$, $0.061 \mu_B/\text{fu}$ and $0.091 \mu_B/\text{fu}$ for $x = 0.0$, 0.1 and 0.2 , respectively, but they are much smaller than the theoretical value of a free Sm^{3+} ion. It may suggest that

nickel has a magnetic moment equal to $0.27 \mu_B$ and this moment is oriented antiparallel to the samarium ion moment. Comparing our results with similar systems such as RT_2 and RT_3 where $R = \text{Gd}, \text{Sm}$, we can see that the Ni atoms have a nonzero value of the magnetic moment between $0.15 \mu_B$ to $0.3 \mu_B$ oriented antiparallel to the rare earth moment [9–11]. The obtained parameters are listed in Table I.

4. Conclusions

We have examined a series of $\text{Sm}(\text{Ni}_{1-x}\text{Co}_x)_3$ compounds with $x = 0.0, 0.1, 0.2$ for their general structural and magnetic properties with an emphasis on the magnetocaloric effect. The chemical substitution and pulverization have a significant impact on the basic physical properties. The substitution of Ni by Co causes an increase in the lattice parameters a and c , the effective moment μ_{eff} , the saturation magnetization M_s , and the entropy change $-\Delta S_M$. Simultaneously, an increase in the Co concentration causes a rapid decrease of the coercivity H_c . The low values of μ_{eff} and M_s suggest the Ni has a magnetic moment μ_{Ni} equal to $0.27 \mu_B$ oriented antiparallel to the Sm moment. A chemical modification consisting of substitution of Ni by Co has enhanced the magnetocaloric properties of the examined materials. The value of the magnetic entropy changes increased approximately two-fold for the doped bulk sample while compared with the undoped one. Mechanical grinding leads to an increase in the saturation and a decrease in the coercivity in all examined samples, together with a great drop of the magnetic entropy changes at the phase transition temperature T_c .

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