Solid State Communications 250 (2017) 14–17

Contents lists available at ScienceDirect

Solid State Communications

journal homepage: www.elsevier.com/locate/ssc

Communication

Comparative studies of magnetic and magnetocaloric properties in amorphous $Gd_{0.67}Y_{0.33}$ and $Gd_{0.67}Zr_{0.33}$ films

G. Alouhmy[a], R. Moubah[a,*], E.H. Sayouty[b], H. Lassri[a]

[a] LPMMAT, Université Hassan II de Casablanca, Faculté des Sciences Ain Chock, BP 5366 Mâarif, Casablanca, Morocco
[b] LPHEMaC, Université Hassan II de Casablanca, Faculté des Sciences Ain Chock, BP 5366 Mâarif, Casablanca, Morocco

ARTICLE INFO

Keywords:
Amorphous Gd-alloys, Spin wave
Magnetocaloric effect
Magnetic entropy change
Magnetic transition, Relative cooling power

ABSTRACT

Amorphous $Gd_{0.67}\times_{0.3}$ (X=Y, Zr) films were grown by RF sputtering and their magnetic and magnetocaloric properties were studied. The magnetic properties were found to be improved in case of $Gd_{0.67}Y_{0.33}$ with respect to $Gd_{0.67}Zr_{0.33,}$ in which the Curie temperature, magnetization and spin wave stiffness were higher for $Gd_{0.67}Y_{0.33}$, which we attribute to its larger Gd-Gd distance. The temperature dependence of magnetic entropy change ($-\Delta S_M$) was calculated from the isothermal magnetization. Under a magnetic field change of 3 T, ($-\Delta S_M$) were found to be 2.14 and 1.12 J/kg K, with corresponding relative cooling power (RCP) of 198.86 and 113.2 J/kg, for $Gd_{0.67}Y_{0.33}$ and $Gd_{0.67}Zr_{0.33}$, respectively. The larger magnetocaloric properties for $Gd_{0.67}Y_{0.33}$ are attributed to its higher magnetization.

1. Introduction

Magnetic refrigeration is an attractive technology due to its high efficiency, and ecological compatibility. The magnetocaloric effect (MCE) is at the basis of this application, which involves a change in temperature of a magnetic material upon the application of a magnetic field [1]. In general, the magnetocaloric effect is determined by the magnetic entropy change $(-\Delta S_M)$, and adiabatic temperature change (ΔT_{ad}) under a magnetic field change (ΔH). These parameters are essential to achieve high magnetic refrigeration efficiency [2]. During last years, intense research activities were devoted to develop new magnetocaloric materials with large $(-\Delta S_M)$ and ΔT_{ad} [3–5]. One can notice that most of the efforts were previously dedicated to study first-order magnetic transition (FOMT) materials, because of their high $(-\Delta S_M)$. However, FOMTs occur in a narrow temperature window and are often accompanied with some non-desirable effects such as: irreversibility of the effect, poor mechanical thermal stability or field hysteresis [6]. It is known that magnetic materials with a second-order phase transition (SOMT) lack a very large $(-\Delta S_M)$, but they do present a very high refrigeration capacity (RC), which is now recognized as a key parameter for achieving high magnetic refrigeration efficiency [7,8]. The other positive advantages of SOMT materials are low magnetic hysteresis, higher electrical resistivity, enhanced corrosion resistance, and tunable T_C by varying the composition [9]. Gadolinium (Gd) and its alloys undergo a SOMT, which make them interesting for magnetic refrigeration. Alloying Gd with Y, Zr offers an advantage due to their similar crystal structure with close lattice parameters. Nevertheless, despite the interesting properties of the Gd-(Y, Zr) alloys, all magnetocaloric studies report solely on bulk or crystalline film phases and never in amorphous state. Here, we compare both the magnetic and magnetocaloric properties of amorphous $Gd_{0.67}(Y, Zr)_{0.33}$ films.

2. Experiment

Amorphous $Gd_{0.67}\times_{0.33}$ (X=Y, Zr) films were deposited on glass substrates using composite targets and RF sputtering system. The starting vacuum was 10^{-7} Torr. The used gas during sputtering was Argon of 5N purity. The argon pressure during growth was fixed at 6×10^{-3} Torr, while the RF power was in the range 80–100 W. Water cooled were used during growth to cool down the substrate to stabilize an amorphous state of the samples. Magnetization measurements were carried out using extraction method with an applied external field up to 5 T and in the temperature range of 4.2–220 K [10].

3. Results and discussion

3.1. Magnetic properties

The temperature dependence of magnetization recorded at a magnetic field of 0.5 T for amorphous $Gd_{0.67}Y_{0.33}$ and $Gd_{0.67}Zr_{0.33}$ thin films are shown in Fig. 1. The M(T) curves were recorded in field

* Corresponding author.
E-mail address: reda.moubah@hotmail.fr (R. Moubah).

http://dx.doi.org/10.1016/j.ssc.2016.11.009
Received 31 July 2016; Received in revised form 20 September 2016; Accepted 11 November 2016
Available online 12 November 2016
0038-1098/ © 2016 Elsevier Ltd. All rights reserved.

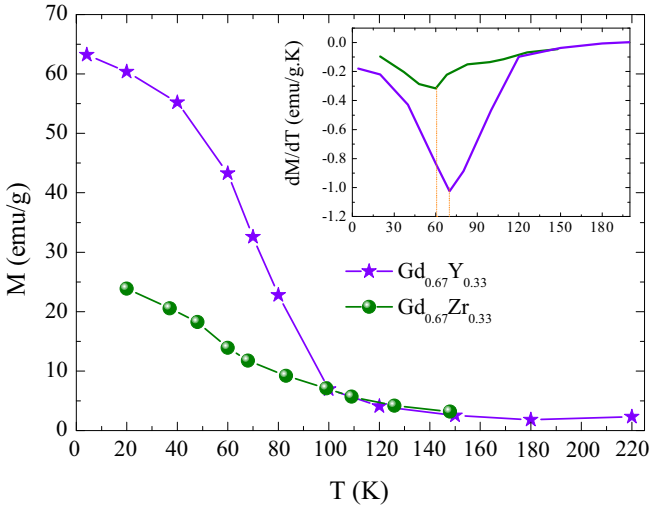

Fig. 1. Change of the magnetization as a function of temperature of the amorphous $Gd_{0.67}Y_{0.33}$ and $Gd_{0.67}Zr_{0.33}$ films. The measurements were recorded at an applied magnetic field of 0.5 T. The inset shows the corresponding $|dM/dT|$ *vs.* T plot.

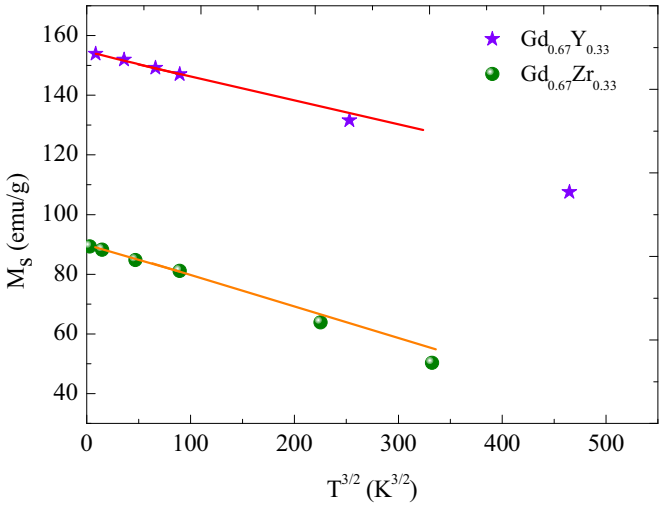

Fig. 2. Change of the magnetization as a function of $T^{3/2}$ of the amorphous $Gd_{0.67}Y_{0.33}$ and $Gd_{0.67}Zr_{0.33}$ films. The measurements were carried out under an applied field of 5 T.

cooling (FC) mode. The samples were cooled down from high to low temperature in the presence of the applied magnetic field and then the measurements were carried out in warming mode from low to high temperature [11]. As can be observed in the figure, both samples show a decrease in magnetization with increasing temperature, which is typical for a ferromagnetic behavior [12]. In order to determine the Curie temperature (T_C), we display in the inset of Fig. 1 the $|\frac{dM}{dT}|$ *vs.* T plot. The T_C is defined as the inflection point of derivative and it is determined to be 70 and 60 K for $Gd_{0.67}Y_{0.33}$ and $Gd_{0.67}Zr_{0.33}$ respectively. These results show that the $Gd_{0.67}Y_{0.33}$ alloy exhibits higher T_C than that of $Gd_{0.67}Zr_{0.33}$. We note that the effective moments of Gd (μ_{eff}^{Gd}) deduced from Curie Weiss law were found to be 7.99 μ_B and 7.92 μ_B for $Gd_{0.67}Y_{0.33}$ and $Gd_{0.67}Zr_{0.33}$, respectively.

For ferromagnetic materials, the temperature dependence of magnetization M (T) follows Block's law ($T^{3/2}$) which is associated to the thermal excitation of spin waves [13,14]. According to the spin wave theory, the M (T) curves of ferromagnetic materials can be expressed using the following formula:

$$\frac{M(0) - M(T)}{M(0)} = BT^{3/2} \quad (1)$$

$$B = 2.612\left[\frac{g\mu_B}{M_0(0)}\right]\left[\frac{k_B}{4\pi D}\right]^{3/2} \quad (2)$$

Where B is the spin–wave constant, μ_B is the Bohr magneton, k_B is the Boltzman constant, D is the spin wave stiffness and g is the Landé factor. Eq. (1) is a good estimate of low-temperature magnetization for crystalline and amorphous ferromagnetic materials [15]. Fig. 2 shows the variation of magnetization as a function of $T^{3/2}$ recorded at a field of 5 T for both alloys. As can be observed, Eq. (1) fits well the low temperature data. The linear fit (solid lines in Fig. 2) of the experimental data permits to determine the B parameter using Eq. (1), which is defined as the slope of the M *vs.* $T^{3/2}$ curve. Finally, the use of the obtained B values and Eq. (2) allows to determine the exchange stiffness constant D (Table 1). As can be observed in Table 1, the D parameter is found to be larger for the $Gd_{0.67}Y_{0.33}$ alloy highlighting that the ferromagnetic interaction is higher for this alloy. This is in agreement with the results described above (T_C is higher for $Gd_{0.67}Y_{0.33}$). The increase of the ferromagnetic interaction for the $Gd_{0.67}Y_{0.33}$ alloy can be understood by its longer Gd-Gd interatomic distance due to the larger Y atomic radii with respect to Zr. This larger Gd-Gd interatomic distance should shift the magnetic interaction from antiferromagnetic to ferromagnetic [16,17]. Due to the random

Table 1
Comparison of the parameters extracted using spin wave theory for amorphous $Gd_{0.67}Zr_{0.33}$ and $Gd_{0.67}Y_{0.33}$ alloys.

Sample	B ($K^{-3/2}$)	D (meV.Å^2)	A (erg/cm)	$r_{Gd\text{-}Gd}$ (Å)
$Gd_{0.67}Zr_{0.33}$	1.06 10^{-3}	9.7	5.6 10^{-8}	3.63
$Gd_{0.67}Y_{0.33}$	5 10^{-4}	10.7	4.3 10^{-8}	3.7

distribution of the Gd-Gd distances within the amorphous matrix, the magnetic interaction is not homogenous. At short Gd–Gd distances, the exchange interaction is antiferromagnetic and at large Gd–Gd distances the ferromagnetic interaction is dominant. However, the presence of well-defined T_C indicates that the ferromagnetic interaction is dominant. To estimate the Gd-Gd interatomic distance, we utilize the Heisenberg model. We note that the Heisenberg model can describe the systems presenting localized electrons [18]. The magnetism in gadolinium (Gd) is related to the 4 f bands, which are strongly localized. Therefore, we can safely apply the Heisenberg model for the system studied here. According to Heisenberg model, D and T_C can be expressed as:

$$D = \frac{k_B r_{Gd-Gd}^2 T_c}{2(S_{Gd}+1)} \quad (3)$$

Where $r_{Gd\text{-}Gd}$ is the distance between nearest magnetic atoms (Gd) and S_{Gd} is the spin moment of the Gd atom. Using Eq. (3), we have determined the r_{Gd-Gd} to be about 3.63 and 3.7 Å for $Gd_{0.67}Zr_{0.33}$ $Gd_{0.67}Y_{0.33}$, respectively. These results support that the increase of the ferromagnetic interaction is associated with the larger Gd-Gd interatomic distance for $Gd_{0.67}Y_{0.33}$.

From the coefficient D mentioned above, it is possible to calculate the exchange constant A. We note that A and D are related as:

$$A = \frac{M_0 D}{2g\mu_B} \quad (4)$$

All the extracted parameters obtained using spin wave theory are listed in Table 1.

3.2. Magnetocaloric properties

In order to study the magnetocaloric effect in our samples, we have carried out isothermal magnetization curves recorded at different temperatures [Fig. 3(a) and (b)]. As shown for both $Gd_{0.67}Y_{0.33}$ and $Gd_{0.67}Zr_{0.33}$ alloys, a progressive decrease of magnetization with a linear variation can be seen with increasing temperature, which is due

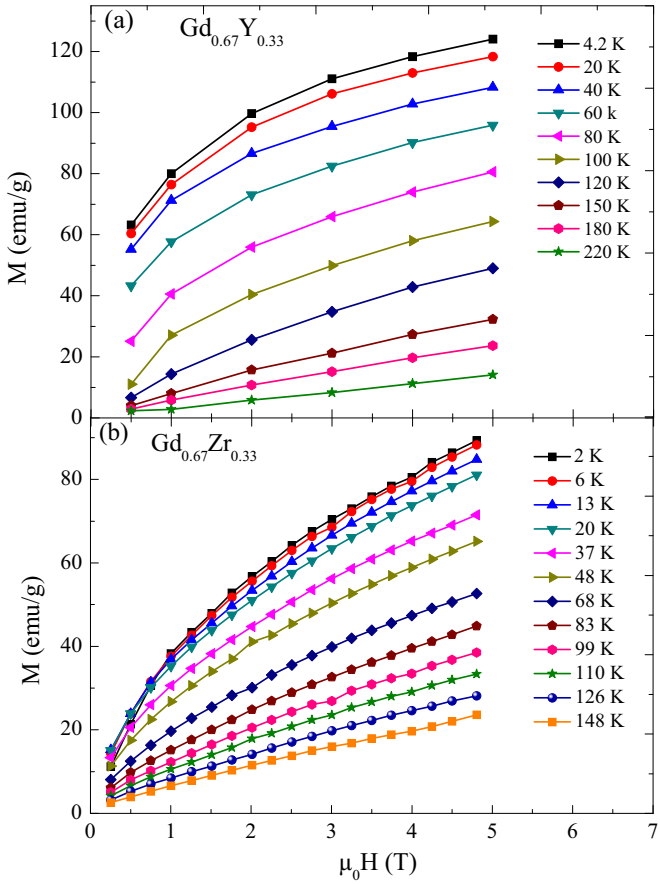

Fig. 3. Isothermal magnetization curves recorded at different temperatures of the amorphous (a) $Gd_{0.67}Y_{0.33}$ and (b) $Gd_{0.67}Zr_{0.33}$ films.

to the ferromagnetic to paramagnetic transition in the vicinity of T_C. We note that the magnetization of $Gd_{0.67}Y_{0.33}$ is higher than that of $Gd_{0.67}Zr_{0.33}$. At a temperature of 4.2 K and for an applied field of 5 T, the magnetizations are found to be 120 and 90 emu/g for the $Gd_{0.67}Y_{0.33}$ and $Gd_{0.67}Zr_{0.33}$ samples, respectively. This shows that Y induces better magnetic properties than Zr. One can notice that the magnetization of samples does not saturate even at a field up to 5 T, which can be explained by the existence of antiferromagnetic interactions.

Using Maxwell relation, $(-\Delta S_M)$ can be calculated from the isothermal magnetization curves in the vicinity of T_C. From the thermodynamic theory, the magnetic entropy change caused by the change of the external magnetic field from 0 to H_{max} can be expressed as:

$$\Delta S_M(T, \Delta H) = S_M(T, H) - S_M(T, 0) = \int_0^{H_{MAX}} \left(\frac{\partial M}{\partial T}\right)_T dH$$

In case of discrete change of applied fields, we use the following formula [19]:

$$\Delta S_M = \sum_i \frac{M_{i+1} - M_i}{T_{i+1} - T_i} \Delta H_i \quad (5)$$

Where M_i and M_{i+1} are the experimental values of magnetization at temperatures Ti and T_{i+1} under an applied magnetic field H_i, respectively [20].

The results of the temperature dependence of $(-\Delta S_M)$ for $Gd_{0.67}Zr_{0.33}$ and $Gd_{0.67}Y_{0.33}$ are displayed in Fig. 4. For both alloys, $(-\Delta S_M)$ increases with increasing temperature to reach a broad maximum around T_C. The caret-like shape of the $(-\Delta S_M)(T)$ curves shows that the magnetic transition near T_C is a second-order phase transition. It is observed that the value of $(-\Delta S_M)$ for $Gd_{0.67}Y_{0.33}$ is

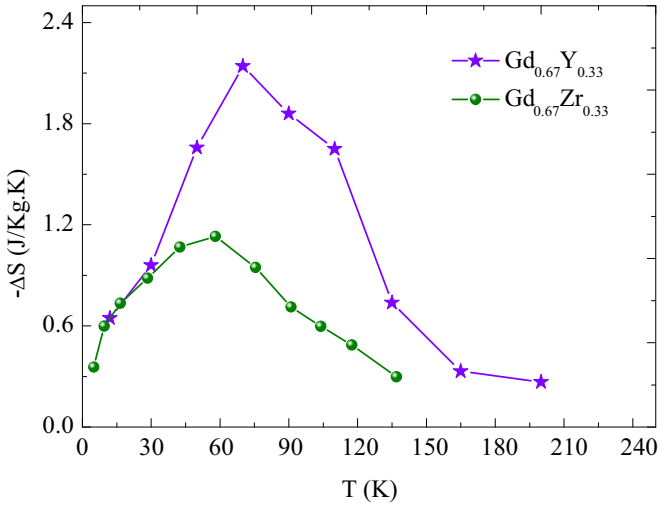

Fig. 4. Magnetic entropy changes as a function of temperature of the amorphous $Gd_{0.67}Y_{0.33}$ and $Gd_{0.67}Zr_{0.33}$ films obtained at a magnetic field change of 3 T.

higher than that of $Gd_{0.67}Zr_{0.33}$. For a field change of 3 T, $(-\Delta S_M)$ are found to be 2.14 and 1.12 J/kg. K, for $Gd_{0.67}Y_{0.33}$ and $Gd_{0.67}Zr_{0.33}$ alloys, respectively. The larger value of of $(-\Delta S_M)$ for the $Gd_{0.67}Y_{0.33}$ alloy can be understood by its larger magnetization with respect to $Gd_{0.67}Zr_{0.33}$ (Fig. 3).

Note that a large $(-\Delta S_M)$ is not enough to obtain excellent magnetic refrigeration features. The effective method for characterizing the cooling efficiency is the RCP which is defined as:

$$RCP = (-\Delta S_M) * \delta T_{FWHM} \quad (6)$$

Where δT_{FWHM} is the full width at half-maximum of the $(-\Delta S_M)(T)$ curve [21]. The RCP of a magnetic material is a measure of how much heat is transferred between the hot and cold ends in one ideal refrigeration cycle and it is an important parameter as far as the magnetic cooling is concerned. The changes of RCP as function of the applied magnetic field for the amorphous $Gd_{0.67}Zr_{0.33}$ and $Gd_{0.67}Y_{0.33}$ alloys are shown in Fig. 5. As can be observed for both samples, the RCP increases with increasing magnetic field. $(-\Delta S_M)$ spans over a wide temperature window. Under a field change of 3 T, δT_{FWHM} are about 92.88 and 100.08 K, with corresponding RCP values of 198.86 and 113.2 J/kg for $Gd_{0.67}Y_{0.33}$ and $Gd_{0.67}Zr_{0.33}$ alloys, respectively. $Gd_{0.67}Y_{0.33}$ alloy exhibits a larger RCP than $Gd_{0.67}Y_{0.33}$ due to its higher $(-\Delta S_M)$. Thus, we can conclude that the Gd-Y alloys present

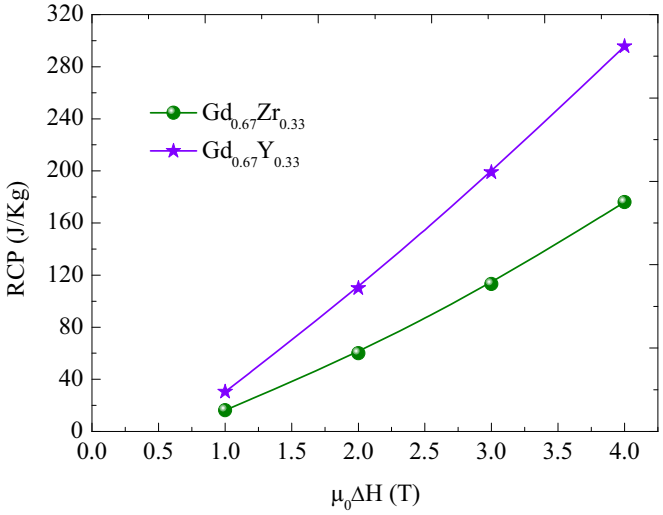

Fig. 5. Change of the relative cooling power (RCP) as a function of the applied field for amorphous $Gd_{0.67}Zr_{0.33}$ and $Gd_{0.67}Y_{0.33}$ alloys.

better magnetocaloric performance than Gd-Zr.

4. Conclusion

In summary, the magnetic and magnetocaloric properties of amorphous $Gd_{0.67}(Y, Zr)_{0.33}$ alloys were studied. Magnetic measurements have shown the existence of a ferromagnetic order with Curie temperature of 70 and 60 K for $Gd_{0.67}Y_{0.33}$ and $Gd_{0.67}Zr_{0.33}$ respectively. The spin wave theory allowed us to find that the ferromagnetic interactions are stronger for the $Gd_{0.67}Y_{0.33}$ due to its longer Gd-Gd interatomic distance. For a magnetic field change of 3 T, $Gd_{0.67}Y_{0.33}$ and $Gd_{0.67}Zr_{0.33}$ have a maximum magnetic entropy value of 2.141 and 1.12 J/kg K, with RCP values of 198.86 and 113.2J/kg, respectively. Finally, our comparison shows that $Gd_{0.67}Y_{0.33}$ is more interesting than $Gd_{0.67}Zr_{0.33}$ for achieving both good magnetic and magnetocaloric properties.

Acknowledgment

Financial support from the PHC Maghreb 15MAG07 is gratefully acknowledged.

References

[1] B. Podmilsak, J.-K. Kim, P.J. McGuiness, S. Kobe, J. Alloy. Compd. 591 (2014) 29.
[2] A. Bhattacharyya, S. Giri, S. Majumdar, J. Magn. Magn. Mater. 323 (2011) 1484.
[3] R. Moubah, A. Boutahar, H. Lassri, A. Dinia, S. Colis, B. Hjörvarsson, P.E. Jönsson, Mater. Lett. 175 (2016) 5.
[4] A. Ben Hassine, A. Dhahri, L. Bouazizi, M. Oumezzine, E.K. Hlil, Solid State Commun. 233 (2016) 6.
[5] X. Si, Y. Liu, W. Lei, J. Xu, W. Du, J. Lin, T. Zhou, X. Lu, Solid State Commun. 247 (2016) 27.
[6] F. Guillou, G. Porcari, H. Yibole, N. van Dijk, E. Brück, Adv. Mater. 26 (2014) 2671.
[7] P. Gorria, J.L.S. Llamazares, P. Álvarez, M.J. Pérez, J.S. Marcos, J.A. Blanco, J. Phys. D: Appl. Phys. 41 (2008) 192003.
[8] Y. Liu, J. Zhang, Y. Wang, Y. Zhu, Z. Yang, J. Chen, S. Cao, Appl. Phys. Lett. 94 (2009) 112507.
[9] L. Li, H. Igawa, K. Nishimura, D. Huo, J. Appl. Phys. 109 (2011) 083901.
[10] E. Loudghiri, K. Roky, A. Hassini, A. Belayachi, H. Lassri, Physica B 353 (2004) 53.
[11] R. Moubah, S. Colis, C. Ulhaq-Bouillet, M. Drillon, A. Dinia, J. Phys.: Cond. Matter 23 (2011) 276002.
[12] Y. Liu, J. Zhang, S. Cao, Z. Ren, J. Appl. Phys. 104 (2008) 043901.
[13] A. Ettayfi, R. Moubah, E.K. Hlil, S. Colis, M. Lenertz, A. Dinia, H. Lassri, J. Magn. Magn. Mater. 409 (2016) 34.
[14] F. Lmai, R. Moubah, A. El Amiri, Y. Abid, I. Soumahoro, N. Hassanain, S. Colis, G. Schmerber, A. Dinia, H. Lassri, Opt. Mater. 57 (2016) 28.
[15] R. Moubah, A. Fnidiki, N. Omari, M. Abid, E.K. Hlil, H. Lassri, J. Supercond. Nov. Magn. 28 (2015) 2149.
[16] W. Fang, Y. Liu, B. Guo, L. Peng, Y. Zhong, J. Zhang, Z. Zhao, J. Alloy. Compd. 584 (2014) 240.
[17] A. Zamani, R. Moubah, M. Ahlberg, H. Stopfel, U.B. Arnalds, A. Hallén, B. Hjörvarsson, G. Andersson, P.E. Jönsson, J. Appl. Phys. 117 (2015) 143903.
[18] W. Nolting, A. Ramakanth, Quantum Theory of Magnetism, edition, Springer, 2010.
[19] A. Ettayfi, R. Moubah, A. Boutahar, E.K. Hlil, H. Lassri, J. Supercond. Nov. Magn. 29 (2016) 133.
[20] A. Waske, B. Schwarz, N. Mattern, J. Eckert, J. Magn. Magn. Mater. 329 (2013) 101.
[21] H. Shen, H. Wang, J. Liu, D. Xing, F. Qin, F. Cao, D. Chen, Y. Liu, J. Sun, J. Alloy. Compd. 603 (2014) 167.