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# Magnetic Characterization and Thermal Stability of Gd<sub>50</sub>Co<sub>48</sub>Fe<sub>2</sub> Metallic Glass

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Solid phase stability and magneto-caloric effect of a ternary Gd<sub>50</sub>Co<sub>48</sub>Fe<sub>2</sub> amorphous as-spun ribbons was studied in this work. The magnetization curve was measured at temperature range from 200 to 360 K. Subsequently the isothermal magnetization curves were measured as well at temperatures ranging from 200 to 350 K and at magnetic field between 1 to 5 T, using SQUID. Based on these experimental data, the magnetic entropy changes were determined. Thermal stability and phase composition of amorphous alloy was experimentally confirmed by difference scanning calorimetry and synchrotron X-ray diffraction. At elevated temperatures two crystallization events were observed. It has been found that the investigated alloy is a prospective aspirant for magnetic cooling devices.

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## 1. Introduction

The traditional vapor-cycle refrigeration needs tens of thousands ton of environmentally harmful coolants every year. This trend is a cause for concern in connection with the global warming and the ever increasing global consumption of energy in recent years. Therefore, in the last few decades there has been a lot of active research on new cooling technologies. One of them is the magnetic refrigeration (MR) technology based on the magneto-caloric effect (MCE). Compared to conventional gas refrigerants, MR have the following advantages: they are safe for the environment, have reduced energy costs, are more efficient, and more compact. Advancing this technology requires materials that will have a MCE in a wide temperature range. In this regard, many magnetic materials with excellent MCE have been developed in the last few decades [1–3].

Amorphous materials that undergo a second order magnetic phase transition are particularly interesting among MCE materials. Metallic glasses (MG) seem to be ideal candidates for MR because they usually exhibit large entropy change ( $\Delta S_m$ ), and broad distribution of the  $\Delta S_m$  peak, which are very good for practical applications, as the MCE can thus be used over a larger temperature range. In contrast, the crystalline alloys with MCE has narrower  $\Delta S_m$  peak, because they undergo

first-order magnetic phase transition [4]. In addition, amorphous alloys have ultrahigh refrigeration capacity, ultralow magnetic hysteresis, better corrosion resistance, and mechanical properties.

MCE has been found to be quite large in Gd-Co-based MG [1, 2, 4]. Also, the change in the chemical composition in these samples affects the magnetic ordering temperature, which makes it possible to use them for wide range of temperatures for applications [5]. Recent researches [6] show that Gd<sub>50</sub>Co<sub>48</sub>Fe<sub>2</sub> MG are interesting choice for the active magnetic refrigerants working at near-room temperature. However, thermal stability of these samples were not investigated in any of the works. The goals of the present study were to fabricate amorphous Gd<sub>50</sub>Co<sub>48</sub>Fe<sub>2</sub> alloy, verify large magnetocaloric effect exhibited at room temperature, and provide information about its thermal stability and phase composition.

## 2. General information

For the alloy preparation gadolinium, cobalt, and iron elements of high purity, all above 99.9%, were used. The Mini Arc Melting System MAM-1 was used in order to prepare a master ingot of the Gd<sub>50</sub>Co<sub>48</sub>Fe<sub>2</sub> at.% in form of buttons. The master ingot was inductively heated to the temperature of 1930 K, which is well above melting point of the alloy (1811 K), quenched down by splashing the melt on a surface of Cu wheel rotating with surface velocity of 30 m/s. The final sample after melt spinning was produced in form of ribbon of thickness of  $\approx 35 \mu\text{m}$  and width of  $\approx 4 \text{ mm}$ . Surface topology and chemical composition of the sample

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were analysed using the scanning electron microscope (SEM) Tescan Vega-3 XMU equipped with SDD Oxford Instruments energy-dispersive spectroscopy (EDS) detector. The magnetic properties of the amorphous ribbon were measured by a superconducting quantum interference device (SQUID) magnetometer MPMS3 made by Quantum Design. Power-compensated differential scanning calorimeter (Perkin Elmer DSC 8000) was used to investigate thermal behaviour of the alloy by applying continuous-heating at heating rates of 5, 10, and 50 K/min. To follow structural evolution a hard X-ray diffraction experiment was performed at the beamline I15-1 located at the Diamond Light Source UK. During the experiment, monochromatic synchrotron radiation of photon energy 80.150 keV ( $\lambda = 0.015469$  nm) was applied. X-ray diffraction data were continuously collected by a large area detector Perkin Elmer XRD 4343 CT during the sample heating from room temperature to 900 K using a hot air blower.

### 3. Results and discussion

Surface topology and chemical composition of the  $Gd_{50}Co_{48}Fe_2$  alloy was investigated on both sides using the SEM equipped with EDS detector. The viewed surface is rough with visible elongated cavities originating from argon gas used in pushing melt out of the quartz ampoule. EDS analysis confirms composition of the alloy  $Gd_{49.17}Co_{48.60}Fe_{2.23}$  which is in very good agreement with our intention.

To study the magnetothermal properties, the magnetization of the amorphous alloys was measured. The temperature dependence of zero field cooled (ZFC) and field cooled (FC) magnetization ( $M-T$ ) curves of the  $Gd_{50}Co_{48}Fe_2$  amorphous ribbon is shown in Fig. 1. The  $M-T$  curve was measured in the range from 200 K to 350 K, at heating rate of 10 K/min. The Curie temperature  $T_C$  of our  $Gd_{50}Co_{48}Fe_2$  amorphous alloy is about 280.8 K, 7 K above freezing point of water.

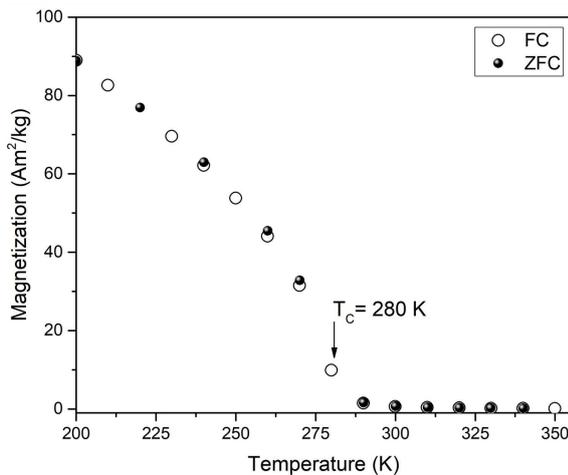


Fig. 1.  $M-T$  curve of the  $Gd_{50}Co_{48}Fe_2$  amorphous ribbons.

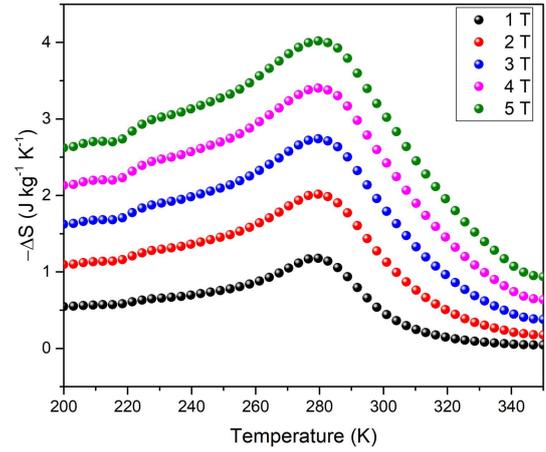


Fig. 2.  $(-\Delta S_m)-T$  curves of  $Gd_{50}Co_{48}Fe_2$  amorphous ribbon at the adiabatic magnetization from zero to different final magnetic field.

TABLE I

The  $(-\Delta S_m^{\max})$  under different magnetic fields.

	1 T	2 T	3 T	4 T	5 T
$-\Delta S_m^{\max}$ [J/(kg K)]	1.19	2.01	2.76	3.41	4.03

The isothermal magnetization ( $M-H$ ) of the alloy at different temperatures ranging from 200 K to 310 K has been measured as well. The temperature dependence of the magnetic entropy change  $(-\Delta S_m)-T$  curves for these amorphous ribbons can be derived from the  $M-H$  curves, according to the thermodynamic Maxwell equation

$$\Delta S_H = \int_0^H \left( \frac{\partial M}{\partial T} \right)_H dH.$$

Figure 2 shows the  $(-\Delta S_m)-T$  curves of the  $Gd_{50}Co_{48}Fe_2$  amorphous alloy at the adiabatic magnetization and final fields in the range of 1 T to 5 T. The  $(-\Delta S_m)$  maximum values of these amorphous ribbons at final fields are listed in Table I. For these samples, negative values of the parameter are observed, which is typical for ferromagnetic materials.

In order to examine thermal stability and structural evolution of the  $Gd_{50}Co_{48}Fe_2$  amorphous alloy, two types of experiments were performed, conventional differential scanning calorimetry (DSC) measurement and *in situ* high temperature X-ray diffraction (XRD) experiment. Results of the two inherently different experiments are compared in Fig. 3. Figure 3a shows the 3D plot demonstrating changes of the  $Gd_{50}Co_{48}Fe_2$  X-ray structure factors with temperature. This data confirms that quenched sample is fully amorphous. The plot covering temperature interval of 300–900 K displays progressive transformation of the originally rapidly solidified sample through crystallization and subsequent transformation stages.

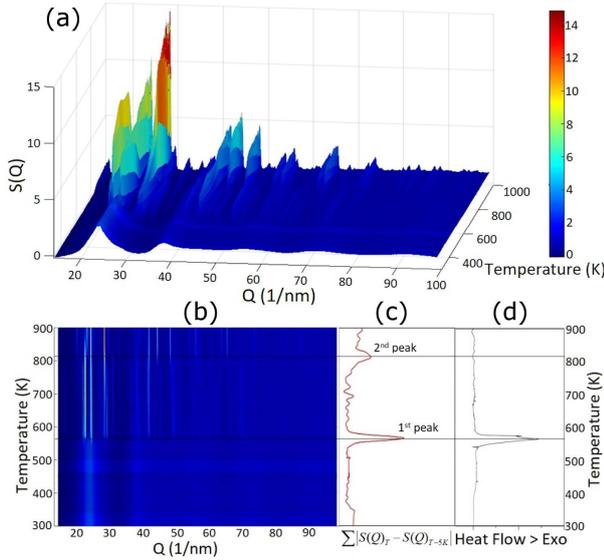


Fig. 3. (a) 3D plot of the  $Gd_{50}Co_{48}Fe_2$  X-ray structure factors as function of temperature, (b) contour plot, (c) instant structure factor change after sample temperature increased by 5 K, (d) DSC heat flow vs. temperature record.

TABLE II

Significant temperatures of the  $Gd_{50}Co_{48}Fe_2$  obtained from DSC curves for different heating rates.

Heating rate [K/min]	$T_g$ [K]	$T_{X\text{ onset}}$ [K]	$T_{x1}$ [K]	$T_{x2}$ [K]	$T_{x2\text{ out}}$ [K]	$T_{\text{trans}}$ [K]	$T_{\text{trans}2}$ [K]
5		535	553	566	568	937	991
10	391	540	558	572	576	943	1001
50	400	530	533	584	596	946	

Figure 3b is the same as 3a, but viewed from the top, which is the so-called contour plot representation. Figure 3c shows quantification of how much the structure is changed by increasing sample temperature by 5 K increments. Such a type of plot and analysis has been invented by our group and it was presented for first time in the article Michalik et al. [7]. The notable feature of the instant structural change representation/analysis is the fact that it provides outputs that are very comparable to the calorimetric signal. The figures show several characteristic sample transformations occurring at characteristic temperatures. DSC curves of the as-quenched alloys measured at heating rate 5, 10, and 50 K/min. All important parameters obtained from the DSC curves are listed in Table II. The glass transition temperature ( $T_g$ ) of the  $Gd_{50}Co_{48}Fe_2$  metallic glass is not very pronounced, but visible at 391 K with heating rate of 10 K/min. After a glass transition, the sample undergoes crystallizations which are clearly visible on the DSC curve by the presence of exothermic peak. Figure 3c shows the phase transformation at temperature of 813 K, not visible in Fig. 3d.

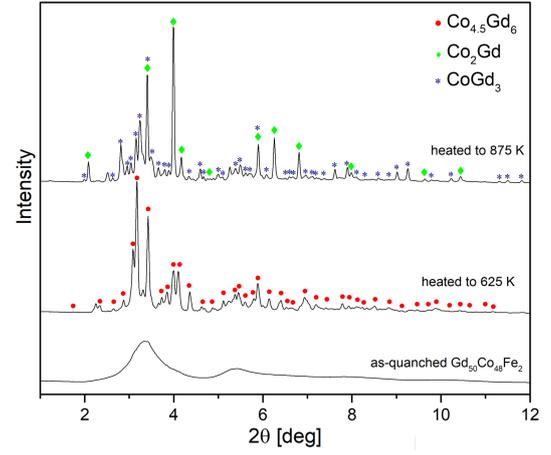


Fig. 4. XRD profiles of as-quenched  $Gd_{50}Co_{48}Fe_2$  ribbon and heated to 625 K and 875 K.

X-ray diffraction patterns of the sample, annealed to the temperatures above the phase transformations, are shown in Fig. 4.

The amorphous phase is stable up to 558 K. Starting from this temperature, the sample begins to crystallize. The first phase, achieved through the crystallization of the amorphous alloy, is the hexagonal close packed  $Co_{4.5}Gd_6$  phase with space group number  $P63/m$ . The phase is stable in the temperature range of 570–830 K. The second transformation of the alloy occurs around 830 K. At this temperature, the face centred cubic  $Co_2Gd$  phase (space group  $Fd-3m$ ) and the orthorhombic  $CoGd_3$  phase (space group  $Pn-ma$ ) appears. The phases are stable in the temperature range between 780 K and 932 K. Beyond the temperature of 932 K, the alloy begins to melt.

#### 4. Conclusions

Goals of present study were to prepare the  $Gd_{50}Co_{48}Fe_2$  alloy, demonstrate the large MCE at room temperature, and contribute to information about phase stability of the alloy. The alloy was prepared into form of as-spun ribbons, of thickness above 35  $\mu\text{m}$ . The Curie temperature ( $T_C = 280.8$  K) was obtained from temperature dependence of magnetization curve. Isothermal magnetization curves at temperature interval 200–350 K were used as a base for calculation of  $(-\Delta S_m)$ , which refers to magnetocaloric behaviour. These curves were measured under different magnetic fields, with the highest  $-\Delta S_m^{\text{peak}} = 4.09$  J/(kg K) value at 5 T. Calculated  $-\Delta S_m^{\text{peak}}$  at all applied fields was achieved at 279 K. DSC and *in situ* synchrotron diffraction experiments proved the amorphous nature of  $Gd_{50}Co_{48}Fe_2$ , with  $T_g$  at 391 K and two crystallization events at 558 and 572 K. All of the above results indicate that amorphous  $Gd_{50}Co_{48}Fe_2$  is one of the possible candidates for application as a magnetic refrigerant around the freezing point of water.

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