Influence of processing parameters on structural and magnetic properties of the $Gd_{5.09}Ge_{2.03}Si_{1.88}$ compound

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Abstract

In this work we present a magnetic and structural characterization of $Gd_{5.09}Ge_{2.03}Si_{1.88}$ compound, analyzing the as-cast bulk, the powder pressed in tablets and sintered and the magnetic behavior of the tablets after some heat treatments. The Rietveld refinements for X-rays diffraction data indicate a negligible change on the lattice parameters (< 0.5%). Sintered tablets present an orthorhombic structure and a small amount of the monoclinic phase (< 6%) induced by the sintering process at 1100^{o}C. The powder of the as-cast sample, which presents a first-order magnetic transition at around 272 K and a second-order one at around 302 K, shows no change when submitted to different compaction pressures for making a tablet. After sintering the tablet at 1100^{o}C, the first-order transition disappears and increasing the compaction pressure for making the tablets, the second-order

transition temperature decreases. A strong correlation between the Curie temperature and the crystallite size indicates that the compaction pressure alters the magnetic properties via the magnetoelastic effect and the structural defects induced by the sintering process. The heat treatments at 1300^{o}C carried out to recover the optimum magnetocaloric properties typical for this compound are not effective.

Introduction

In 1997 V. K. Pecharsky and K. A. Gschneidner Jr. reported the giant magnetocaloric effect in the $Gd_5Ge_2Si_2$ compound [1,2] and in other compounds of the family $Gd_5(Ge_xSi_{1-x})_4$ [3]. As shown by these researchers [3], from this family of materials, the $Gd_5Ge_2Si_2$ compound is not the one that presents the greatest magnetocaloric effect (MCE), described by the quantity ΔS_{mag} (isothermal variation of entropy), however it presents this effect around room temperature. This fact makes $Gd_5Ge_2Si_2$ a potential candidate to be used as a refrigerant material in a magnetic refrigerator that eventually will substitute our conventional refrigerators and air-conditioning devices.

According to Pecharsky and Gschneidner, the as-cast $Gd_5Ge_2Si_2$ presents two magnetic transitions, one of first-order nature around 277 K, due to a majority phase, and another of second-order nature around 300 K, due to a minority phase [4]. Repeating the preparation procedures adopted by them, but using commercial (low purity) gadolinium, we do not obtain the same results. Our as-prepared $Gd_5Ge_2Si_2$ compound presents only the second-order transition at 300 K. To obtain the first-order transition, the one of lowest temperature, it is necessary to carry out heat treatments [5].

When we performed metallographic and WDS (Wavelenght Dispersive Spectroscopy) analyses, we verified that our $Gd_5Ge_2Si_2$ compound presents two

crystallographic phases: the majority phase, with stoichiometry $Gd_{5.09}Ge_{2.03}Si_{1.88}$, and the minority one, with stoichiometry $Gd_{4.59}Ge_{1.74}Si_{2.67}$ [6]. Then, we have decided to prepare an alloy with the stoichiometry of the majority phase of $Gd_5Ge_2Si_2$, i. e., $Gd_{5.09}Ge_{2.03}Si_{1.88}$. As happens with the $Gd_5Ge_2Si_2$ stoichiometry, this new alloy does not present a single phase. Nevertheless, the most important experimental observation is that, even in the as-cast condition, the $Gd_{5.09}Ge_{2.03}Si_{1.88}$ alloy presents the two magnetic transitions, first and second-order ones, as it occurs in Pecharsky and Gschneidner's $Gd_5Ge_2Si_2$ compound. More important, the first order transition is much stronger than the second order one.

It is important to remark that the $Gd_{5.09}Ge_{2.03}Si_{1.88}$ alloy, as well as other magnetocaloric materials reported in the literature, certainly will not be used in their unmanufactured as-cast condition in future magnetic refrigeration applications. To use these materials as magnetic active regenerators it will be necessary to process them into forms dictated by the design of the machine, as wires, thin plates, spheres or other convenient shapes. As this particular compound is very hard and brittle, we considered the use of the techniques of powder metallurgy in order to prepare simple shapes of the material. Our first choice was to grind the as-cast material, sieve it into convenient powder particle sizes, press a small disc of the material (what we will refer to as a tablet) and then sinter this tablet in order to have the final tablet into a consolidated piece. Of course, we established a research program so that the magnetic properties of the material at all stages of preparation were measured and compared with the properties of the as-cast material. The obtained results suggested to do X-rays diffraction measurements to follow the eventual changes in the material was undergoing on the different preparation stages. This work reports our main results obtained for powders of the $Gd_{5.09}Ge_{2.03}Si_{1.88}$ compound.

Experimental procedure

The $Gd_{5,09}Ge_{2,03}Si_{1,88}$ sample was prepared from 99.9 wt.% Gd and with electronic grade Ge and Si by arc-melting three times to guarantee homogeneity. The mass of the sample was 5 g. The sample was then manually crushed and put into powder form. The resulting powder was sieved to obtain powder particles smaller than 50 μm. This powder was pressed in tablet form using a hardened tool steel die. The compaction pressures were applied using a conventional hydraulic press, and were measured using a calibrated strain gage force cell, able to measure accurately forces up to 5 ton. We used different compaction pressures (1.30, 1.73, 2.17 and 2.60 kbar) to obtain the tablets. This range of compaction pressures is typical of the pressures used to obtain green bodies with enough mechanical strength that allow the easy manipulation of them. The tablets were encapsulated into quartz ampoules under Ar inert atmosphere and sintered at 1100^{o}C for 24 hour using a conventional resistive tubular furnace. Some of the sintered tablets were heat treated at 1300^{o}C for 1, 2 and 11 hours in a RF vacuum furnace equipped with a turbo-molecular pump under vacuum of 10^{-4} mbar.

The powder before application of the compaction pressure, the as-pressed tablets, the pressed and sintered tablets, and the pressed, sintered and heat-treated tablets were separately characterized by X-rays diffraction, metallographic and magnetic analyses.

Magnetic measurements were carried out using a commercial SQUID magnetometer (Quantum Design, model MPMS XL). Magnetization versus temperature data were obtained always in a zero-field cooling – field warming process, i. e., the sample is cooled from room temperature with no applied magnetic field and, when in the ferromagnetic regime, the magnetic field is applied and we perform the magnetization measurements increasing temperature and then decreasing temperature.

The X-rays diffraction data for these samples were collected using Cu Kα radiation between 10 and 100 degrees (2θ) at room temperature using a Philips diffractometer (PW

1710), step size of 0.003^{o} and 3 s of counting time. The crystalline structure refinement of each observed phase in the samples was obtained through the Rietveld method.

Results and Discussions

The magnetization versus temperature data for the powder of the as-cast $Gd_{5,09}Ge_{2,03}Si_{1,88}$ alloy present no relevant difference when compared to the same data for the powder submitted to compaction pressures of 1.3 and 2.6 kbar. The transition temperatures for all these samples are the same (~ 272 K). We note that for the as-cast powder the first order transition is relatively broad and there are traces of the second order transition at around 300 K (see Fig. 1). It is also very evident the thermal hysteresis characteristic of magnetic first order transition. X-rays diffraction data for these powders do not indicate any relevant change in the structure with compaction pressure and reveal a majority monoclinic phase at room temperature, as occurs for the optimally prepared $Gd_5Ge_2Si_2$ alloy of A. O. Pecharsky *et al.* [7].

However, when we carried out magnetization vs. temperature measurements for the sintered samples, we observed a drastic change of behavior when comparing ~~with~~ to the original powder (Fig. 1). For compaction pressure of 1.3 kbar, the first-order transition disappears and the dominant second-order transition occurs around 296 K. This temperature is smaller than the second-order transition temperature for the as-cast powder (302 K). Increasing the compaction pressure to obtain the sintered tablets, the transition temperature decreases until 291 K for compaction pressure of 2.6 kbar. We note that the magnetization vs. temperature curves are relatively sharp and we observe negligible thermal hysteresis for all these second order transitions. In recent works [8-10] it was observed that applying hydrostatic pressure in several compounds of the family $Gd_5(Ge_xSi_{1-x})_4$, including $Gd_5Ge_2Si_2$

[10], the transition temperatures always increase with the increasing hydrostatic pressure, contrary to what is observed in the pressed tablets. It is important to emphasize that the compaction pressures applied to make the tablets are not hydrostatic and are not present during the sintering or the measurements. We also observed that the Curie temperature varies with the compaction pressure in a approximately linear way, as shown in Fig. 2. A linear fit to the experimental data show that the Tc variation rate with compaction pressure is 4.16 K/kbar.

This brings about the question of how the compaction pressure affects the magnetic transition temperatures of this compound. As reported above, the as-pressed tablets present the same structure and magnetic transition temperatures as the as-cast powder, but, when sintered at 1100^{o}C/2hours, the structure changes to orthorhombic and the magnetic transition become second order and its critical temperature changes and decreases linearly with the compaction pressure. We note that the compound is very hard and brittle, so that it is not expected to show any ductility. The behavior observed for the structure and the transition temperatures, however, implies that there is some mechanism by which the elastic energy of the compaction process is stored in the as-pressed compound. At the same time, during the sintering process, this energy is partially or totally released, generating defects that distort permanently the lattice. That contributes, through the strong magnetoelastic effect common to this family of compounds, to the stabilization of the orthorhombic structure, which presents the second order magnetic transition. So, it is expected that this compound must have at least some ductility, and that the defects induced by the compaction pressures are somehow stored in the lattice. The most probable type of defect is dislocations. Another possibility is that the formation of grain boundaries (regions of great density of structural defects) during the sintering process induces the stabilization of the orthorhombic structure through the strong magnetoelastic effect. To better clarify these points we have decided to do Rietveld refinements of the diffraction patterns for the tablets.

X-rays diffraction patterns of $Gd_{5.09}Ge_{2.03}Si_{1.88}$ tablets, made with different compaction pressures and sintered, are shown in Figure 3a for the range $20^o \geq 2\theta \leq 60^o$, which coresponds to the range of the most intense reflections. These samples present diffraction patterns very similar to the one presented by an alloy of equivalent composition [11]. All sintered samples present a majority phase with orthorhombic symmetry and a small amount of monoclinic phase (with space group P1121/a). In Fig. 3b, we present the patterns for the range $30^o \geq 2\theta \leq 35^o$ showing the $(141)_{Mono}$ reflection occurring in all samples. The $(132)_{Ortho}$ and $(231)_{Ortho}$ reflections correspond to characteristic reflections of the orthorhombic phase. The $(141)_{Mono}$ reflection presents a displacement of 0.23% and the $(132)_{Ortho}$ reflection presents a displacement of 0.15% as a function of pressure. This small variation affects the structural parameters (lattice parameters and unit cell volume).

In Fig. 4 we show the Rietveld refinements for the tablets with compaction pressures of 1.30 kbar (Fig. 4a) and 2.60 kbar tablets (Fig.4b), confirming the coexistence of two phases (the minority monoclinic and the majority orthorhombic) for sintered tablets obtained with different compaction pressures. The orthorhombic phase was also detected by Morellon et al. [12] working with an alloy whose composition was similar to ours. For all the samples analyzed in our work the discrepancies between experimental and refined profiles are small ($R_{wp} \leq 0.13$), indicating that the unit cell dimensions are accurately determined and the chosen peak shape function pseudo-Voigt is a good fit for these phases.

The effect of compaction pressure on the lattice parameter is shown in Fig. 5 and Table I for the orthorhombic and monoclinic phases. Results indicate a very small influence of the compaction pressure on the structural parameters for both phases. The major variation on the lattice parameters is observed for the c-axis (0.4 %) of the orthorhombic phase. The unit cell volume also shows little influence of the compaction pressure, presenting a variation

of 0.14 % for the monoclinic phase. The volume fraction of the monoclinic phase is small for all tablets (< 6 %).

It is interesting to notice that the temperature of sintering (1100^{o}C), when it is applied in annealing the as-cast $Gd_5Ge_2Si_2$ in bulk, favors the formation of the monoclinic phase and the magnetic first-order transition. However, in the case of the tablets of $Gd_{5.09}Ge_{2.03}Si_{1.88}$, a similar compound, this temperature for sintering favors the formation of the orthorhombic phase, as verified by the X-rays diffraction patterns, and ~~there~~ the first-order magnetic transition is not observed, certainly due to the small amount of the monoclinic phase present in the samples. A. Yan *et al.* [13] reported changes in the magnetic behavior for $Gd_5Ge_2Si_2$ and $Gd_5Ge_{2.3}Si_{1.7}$ compounds caused by different processing parameters, as the cooling rate from the annealing temperature. Therefore, different processing parameters can yield to very different results and we have to keep this in mind when we are dealing with the $Gd_5(Ge_xSi_{1-x})_4$ system.

Regarding the way of the compaction pressure can modify so remarkably the magnetic properties, we used the Rietveld refinements to obtain information about the structural modifications induced by the compaction pressures and brought forth by the heat-treatment at 1100^{o}C. The first parameter we have looked for was the line width of the most intense reflection of the orthorhombic structure (231). We have observed that as the compaction pressure increases so does the observed line width, as shown in Fig. 6. The increase of the line width is indicative of a build up of structural defects as the compaction pressure increases, and these defects can be of different types, as vacancies, dislocations, grain boundaries, etc. From the Rietveld refinements it is also possible to obtain the average size of the crystallites that comprise the different tablets. We have observed that there is a marked decrease of the crystallite size with compaction pressure, as shown by Fig. 7. The decreased size of these crystallites means that we have more grain boundaries, and so more

structural defects, and this is consistent with the increased line width observed. It is interesting to note that there is a strong correlation between the Curie temperature and both the line width and the crystallite size, as shown in Figs. 8a and 8b. In other words, the compaction pressure changes the mechanical (structural) state of the as-cast powder in such a way that the simply pressed powder continues to show the same structural and magnetic properties as before the application of the pressure. When the tablets are submitted to the heat-treatment at 1100^{o}C, the powder sinters and at the same time releases the energy associated with the compaction pressure, which manifests as the formation of crystallites whose mean size decreases as the compaction pressure increases. These structural defects stabilize the orthorhombic phase, and, possibly through the strong magnetoelastic effect observed for these materials, lower the Curie temperature of the compound in a way directly proportional to the size of the crystallites.

Our results imply that the sintering heat-treatment of the pressed tablets, instead of stabilizing the first order magnetic transition, desirable because of the giant magnetocaloric effect associated to it, stabilizes the second order magnetic transition that presents a smaller MCE. This is frustrating, because a temperature as 1100^{o}C is easily obtained with inexpensive conventional resistive furnaces, and the need of higher temperatures imply the use of more sophisticated furnaces, meaning higher costs for the production of such a material by this route. Anyway, we planned to do higher temperature heat-treatments to see what are the experimental conditions necessary to recover the best properties inherent in this material. We carried out heat treatments at 1300^{o}C for 1, 2 and 11 hours in the tablets obtained with pressures of 1.30 (Fig. 9) and 2.60 kbar (Fig. 10), trying to recover the magnetic properties of the original powder. This temperature was chosen based on the very good results for the magnetic properties and MCE reported for the annealed $Gd_5Ge_2Si_2$ [7]. The lower-temperature transitions reappear in all cases, but with lower temperatures than the as-cast

sample in powder form and generally broader. In the case of the 1.30 kbar tablet, the heat treatments for 1 and 2 hours seem to present better results (Fig. 9). In the case of 2.60 kbar tablet, the three periods of heat treatment yield essentially the same behavior (Fig. 10). More studies about annealing these sintered tablets in other temperatures must be carried out to answer properly the question of how to best recover the optimum magnetocaloric properties of the compound.

Conclusions

X-rays powder diffraction determined a majority monoclinic phase for the base compound, as-cast $Gd_{5.09}Ge_{2.03}Si_{1.88}$, used to prepare the sintered tablets. This technique also confirmed an orthorhombic structure for all the sintered tablets as a function of pressure. It was detected a small amount of monoclinic phase (≤ 6 %) for the sintered tablets. The observed variation of the structural parameters (lattice parameters and unit cell volume) as a function of deformation is very small (< 0.5 %), and can not explain the observed changes of the magnetic properties of the compound.

While compounds of the family $Gd_5(Ge_xSi_{1-x})_4$ have its transition temperatures increased with increasing hydrostatic pressure, the transition temperatures of the sintered tablets of $Gd_{5.09}Ge_{2.03}Si_{1.88}$ decrease at a rate of 4.6 K/kbar when we increase the compaction pressure applied for making these tablets. The sintering of the tablets after application of the compaction pressure induces the formation of lattice defects and decreases markedly the crystallite size of the compound. The strong correlation between the Curie temperature and the size of these crystallites is an indication that the compaction pressure alters the Curie temperature through the magnetoelastic effect that mediates the interaction between the lattice and the magnetic part of the compound.

It is known that for $Gd_5Ge_2Si_2$ the annealing temperature of 1100°C favors the formation of the monoclinic phase, but using this temperature in the sintering process of the $Gd_{5.09}Ge_{2.03}Si_{1.88}$ pressed tablets, the orthorhombic phase is favored. Since only pressing the original powder causes no significant change in its magnetic and structural properties, we can conclude that the orthorhombic phase appears actually due to the sintering process.

The heat treatments done at the higher temperature of 1300°C with the objective of recover the monoclinic phase with its first order magnetic transition and giant magnetocaloric effect were poorly effective for the compaction pressure of 1.30 kbar, and definitely not effective for the compaction pressure of 2.60 kbar. This indicates that higher temperatures must be employed in order to recover the optimum magnetocaloric properties characteristic of this compound.

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Table 1

Pressure (Kbar)	Symmetry	a (Å)	b (Å)	c (Å)	V (Å^3)
1.30	$Pnma_{Orth}$	7.531(1)	14.811(3)	7.804(1)	870.47
	$P1121/a_{Mono}$	7.685(2)	14.004(4)	7.802(3)	840.25
1.73	$Pnma_{Orth}$	7.530(2)	14.806(3)	7.807(1)	870.39
	$P1121/a_{Mono}$	7.688(3)	14.011(4)	7.807(3)	841.00
2.17	$Pnma_{Orth}$	7.533(2)	14.816(3)	7.790(1)	869.48
	$P1121/a_{Mono}$	7.695(3)	14.052(1)	7.792(4)	842.65
2.60	$Pnma_{Orth}$	7.542(3)	14.819(4)	7.764(2)	868.32
	$P1121/a_{Mono}$	7.697(3)	14.021(2)	7.806(4)	842.42

Figure captions

Figure 1: Magnetization versus temperature curves for $Gd_{5.09}Ge_{2.03}Si_{1.88}$ in powder form and for the sintered tablets made with pressures of 1.30, 1.73, 2.17 and 2.60 kbar.

Fig. 2: Curie temperature as a function of compaction pressure for the $Gd_{5.09}Ge_{2.03}Si_{1.88}$ compound tablets.

Figure 3: a) X-ray diffraction patterns for the different compaction pressures and b) reflection $(141)_{Mono}$ of monoclinic phase present on all the sintered tablets.

Figure 4: Rietveld refinement of sintered tablets a) P = 1.30 kbar and b) P = 2.60 kbar.

Figure 5: Lattice parameters and unit cell volume as a function of applied pressure for making the tablets.

Fig. 6: Line width of the most intense reflection line of the rhombohedral structure as a function of compaction pressure.

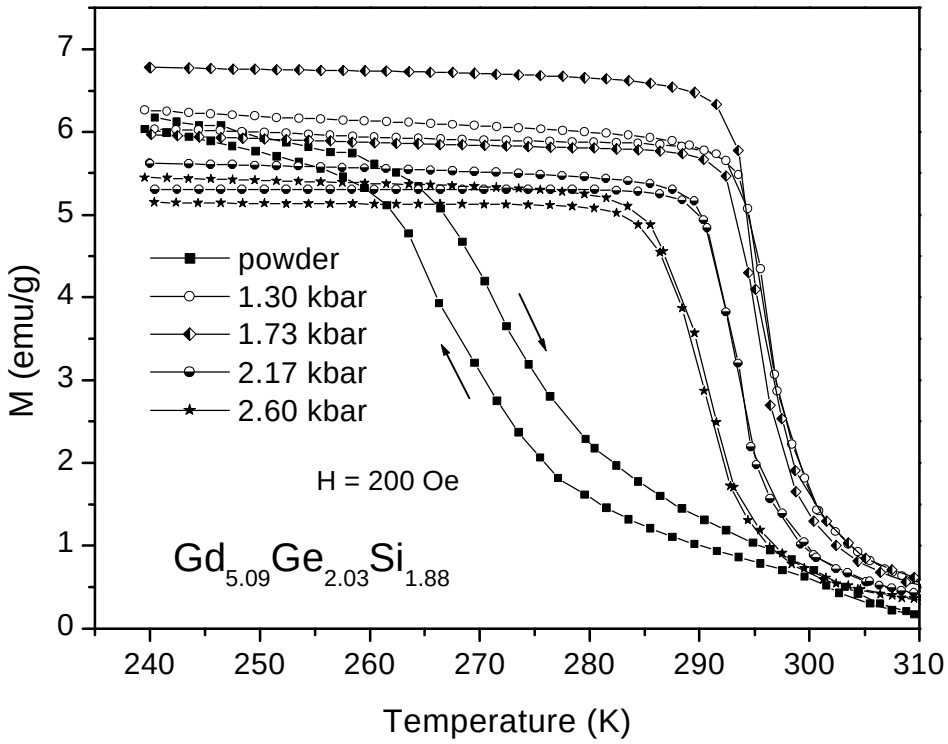
Fig. 7: Crystallite size as a function of compaction pressure for the sintered tablets.

Fig. 8: Dependence of the Curie temperature of the tablets as a function of a) crystallite size; b) line width.

Figure 9: Magnetization versus temperature curves for the sintered tablet, made with pressure of 1.30 kbar (circles), for the sintered tablet annealed in three different conditions (triangles), and comparing with the original powder (squares).

Figure 10: Magnetization versus temperature curves for the sintered tablet, made with pressure of 2.60 kbar (star), for the sintered tablet annealed in three different conditions (triangles), and comparing with the original powder (square).

Figures



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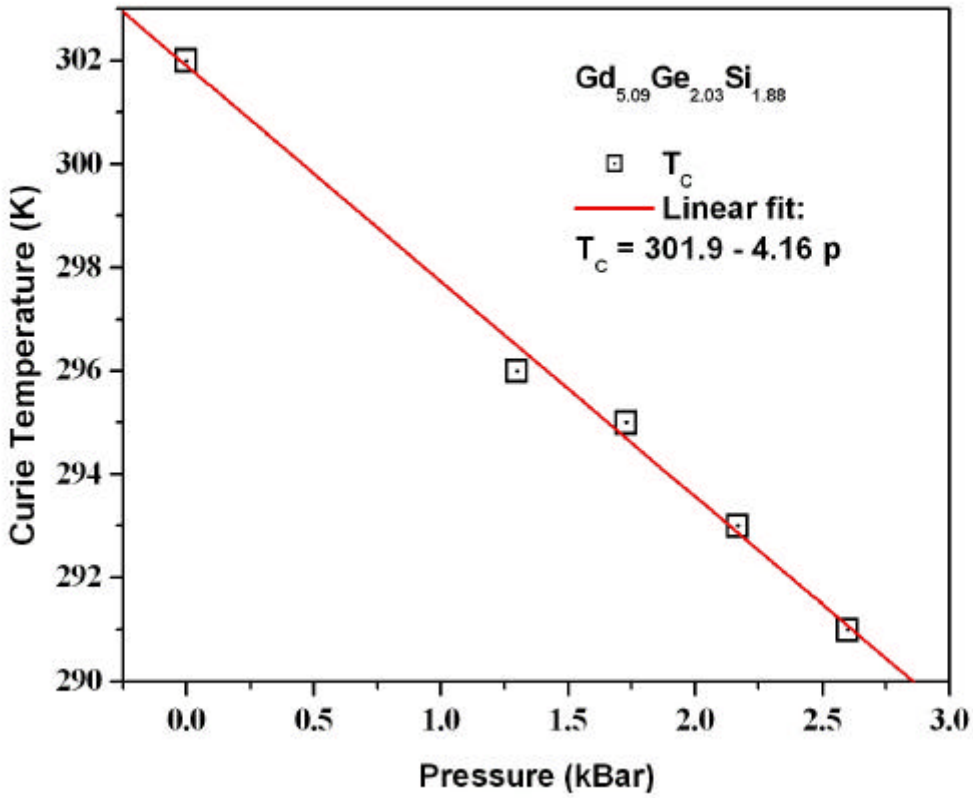


Fig. 2: Curie temperature as a function of compaction pressure for the $Gd_{5.09}Ge_{2.03}Si_{1.88}$ compound tablets.

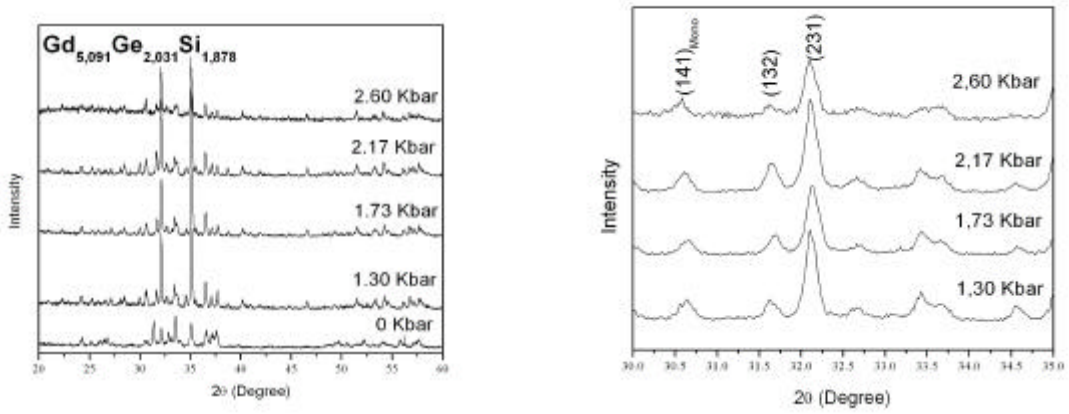


Figure 3: a) X-ray diffraction patterns for the different compaction pressures and b) reflection $(141)_{Mono}$ of monoclinic phase present on all the sintered tablets.

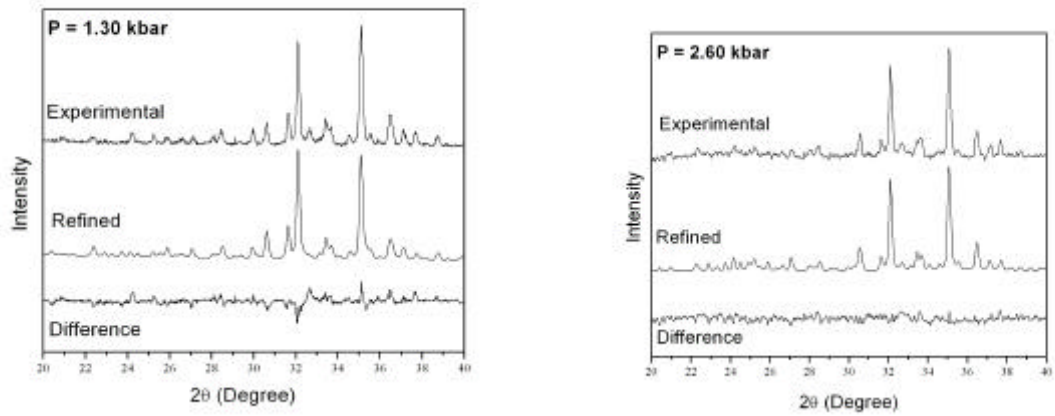


Figure 4: Rietveld refinement of sintered tablets a) P = 1.30 kbar and b) P = 2.60 kbar.

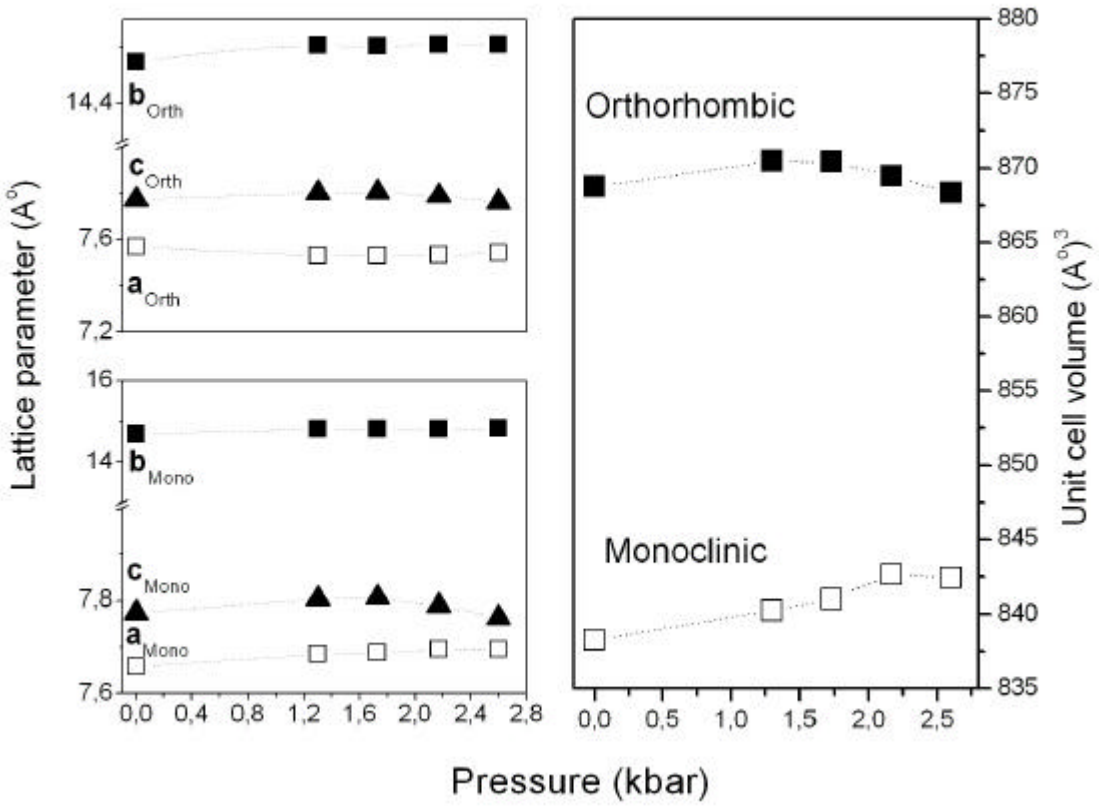


Figure 5: Lattice parameters and unit cell volume as a function of applied pressure for making the tablets.

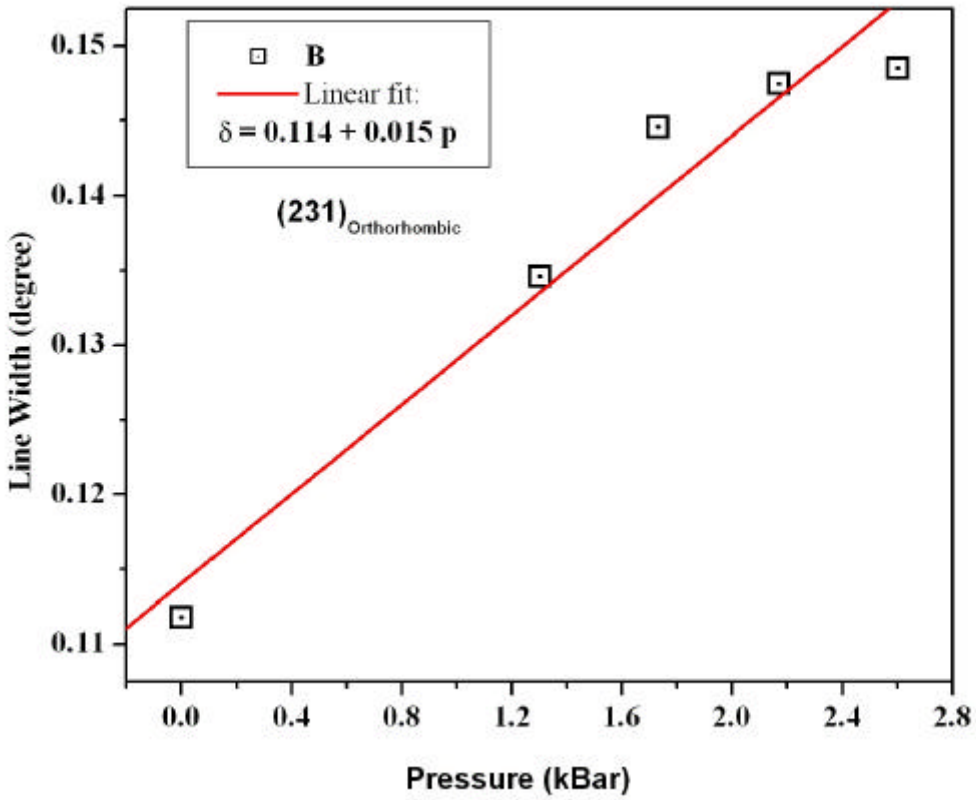


Fig. 6: Line width of the most intense reflection line of the rhombohedral structure as a function of compaction pressure.

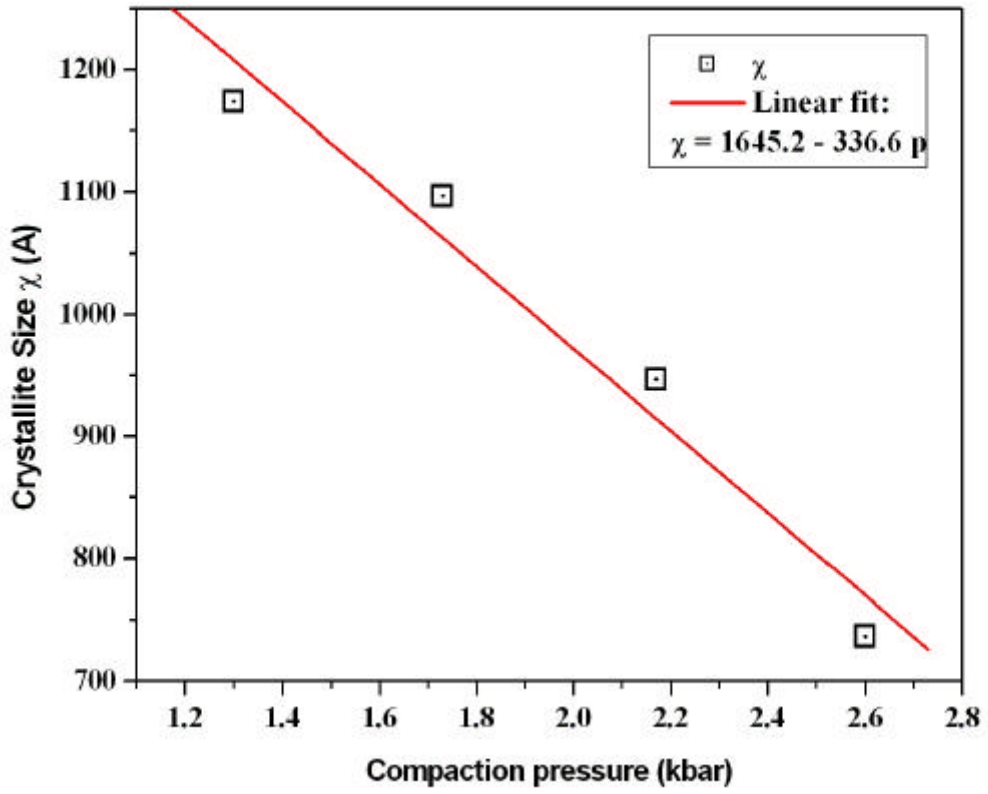


Fig. 7: Crystallite size as a function of compaction pressure for the sintered tablets.

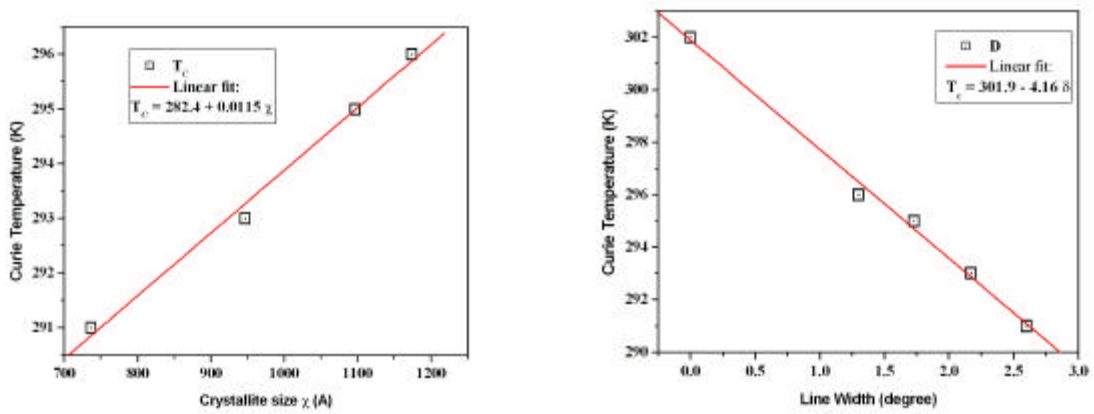


Fig. 8: Dependence of the Curie temperature of the tablets as a function of a) crystallite size; b) line width.

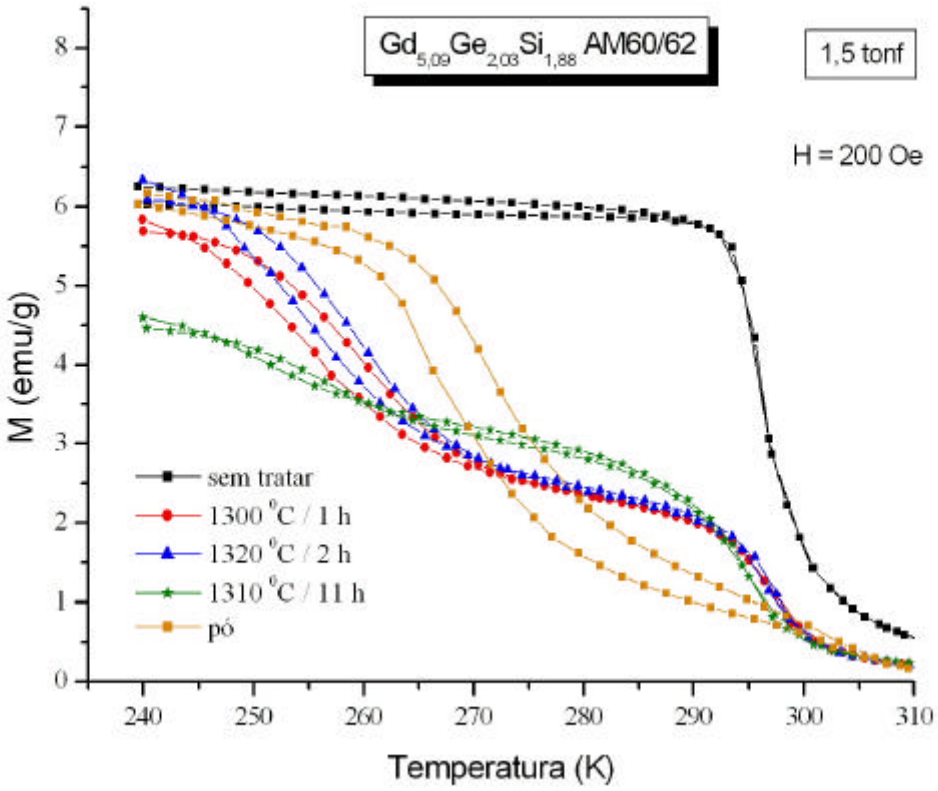
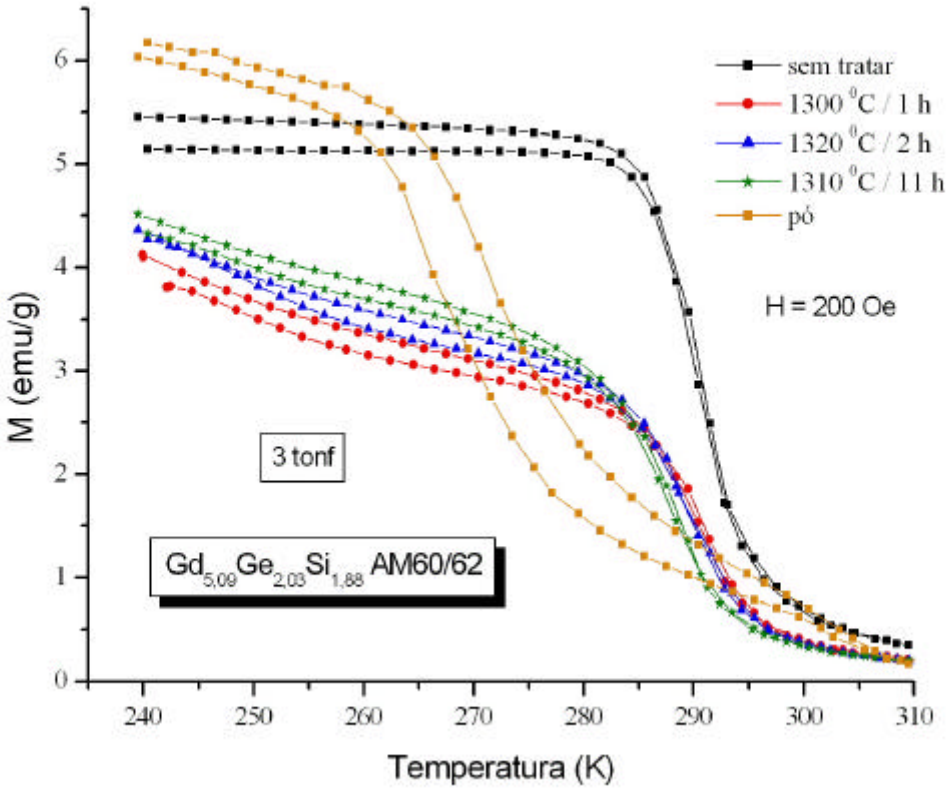


Fig. 9: Magnetization versus temperature curves for the sintered tablet, made with pressure of 1.30 kbar (circles), for the sintered tablet annealed in three different conditions (triangles), and comparing with the original powder (squares).



Fi. 10: Magnetization versus temperature curves for the sintered tablet, made with pressure of 2.60 kbar (star), for the sintered tablet annealed in three different conditions (triangles), and comparing with the original powder (square).