Feasibility of Nd Substitution in (La, Nd)(Fe, Si)$_{13}$ Magnetocaloric Compound Obtained by the Reduction-Diffusion Process

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Quaternary magnetocaloric compound $La_{1-x}Nd_xFe_{11.3}Si_{1.7}$ was synthesized via the so-called reduction–diffusion (RD) process. The RD process was carried out at 1423 K, using Ca as the reducing agent and La and Nd oxides as the precursors to form, together with iron and silicon powder, the desired cubic $NaZn_{13}$-type structure. The main purpose was to study the interchange of La and Nd in terms of process yield, crystal structure parameters and typical magnetic transition temperature [Curie temperature (*Tc*)] associated with the magnetocaloric effect. Microstructural characterization by scanning electron microscopy associated with microprobe energy dispersive spectroscopy and backscattered electron imaging was used to identify morphology and particle size of reaction products, as well as the extent of diffusion reactions. Structural characterization results obtained by X-ray diffraction technique associated with Rietveld refinements show the possibility to obtain almost single-phase $La_{1-x}Nd_xFe_{11.3}Si_{1.7}$, for which x was varied from 0 to 0.5, with reminiscent α-iron phase below 10 wt%. Moreover, the *Tc* of all obtained alloys were inferred from differential scanning calorimetry curves, showing that Nd is an effective alloying element to tune the working temperature in the near-room-temperature magnetic refrigeration.

Index Terms—**La(Fe, Si)$_{13}$, magnetocaloric compounds, Nd substitution, reduction-diffusion (RD) process.**

I. INTRODUCTION

It has been shown in recent years that the intermetallic pseudobinary cubic La1(Fe, Si)$_{13}$ phase (also known as 1:13 phase) is a very promising candidate [1] for magnetic refrigerants fabrication, and it could be considered to replace the well-established Gd-based compounds. The 1:13 phase composed of La, Fe, and Si in the right proportions exhibits a first-order magnetic phase transition such as Gd based compounds, thus generating an expressive variation of the magnetic entropy (ΔS_m) around its Curie temperature (T_C). A high ΔS_m value combined with a reasonable variation of adiabatic temperature (ΔS_{ad}), as well as the ease of T_C tuning in a wide temperature range (from 200 to 350 K), makes the 1:13 phase an excellent candidate for the basis of magnetocaloric materials for magnetic refrigeration [1]–[4].

One common way to tune T_C of the 1:13 phase is by changing the lattice parameters via interstitial or substitutional atoms. Through interstitial modification, hydrogen has been pointed out as the only element capable of producing satisfactory changes in T_C without negatively affecting the magnetocaloric effect (MCE) [4]. Nitrogen and carbon show adverse results, causing a decrease in MCE, reducing the entropy change [5], [6]. On the other hand, various substitutional atoms have been identified as promising candidates for T_C tuning. Al, Co, and Mn introduced on the Fe/Si sites, and Ce, Pr, or Nd on the La sites have been identified as promising substitutional elements for tuning T_C. However, by the substitution of different atoms in the lattice, a different degree of magnetization will follow, therefore leading to a change in MCE properties [2], [7]–[10].

Besides tuning T_C, the synthesis of these compounds is also a challenge, which must be addressed in order to produce a functional magnetic refrigerant. Traditionally, the 1:13 phase is synthesized by conventional arc and induction melting processes, followed by a long annealing treatment [3], [11] in order to obtain a near 1:13 single-phase compound. Since 1:13 phase is a product of a slow peritectic reaction between α-Fe and La-rich liquid phase [12], long-term annealing is necessary, which can take up to 7 days at 1423 K, depending on the phase nominal composition. To circumvent long heat treatments, one alternative is the use of melt-spinning processes followed by quick annealing, producing thin ribbons of 1:13 phase [13]. Other authors apply the powder metallurgy route, i.e., milling, pressing, and sintering processes, on conventionally cast ingots or with pure elements [14], [15]. In this case, the interdiffusion between the powder particles, facilitated by high specific surface energy, generates the 1:13 equilibrium phase with shorter treatments.

Another alternative to reduce processing time on the synthesis of 1:13 phase and thus facilitate industrial upscaling is the reduction–diffusion (RD) process, already employed for Sm–Co compounds used in high-performance permanent magnets manufacturing. This technique has the additional advantage of employing rare-earth oxides as raw material, avoiding the use of more expensive and reactive rare-earth metals, which demands special care on handling and storage. RD was successfully adapted to fabricate 1:13 La–Fe–Si compounds in previous works [16], [17], but feasibility of this process for other RE substitutions was not evaluated.

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Therefore, the main focus of this paper is to evaluate the synthesis of (La, Nd)(Fe, Si)$_{13}$ phase by RD process, with a focus on metallurgical aspects of phase formation for several Nd additions. Nd substitution effect will be addressed by the evaluation of the change in the magnetic transition temperature as a function of added Nd amount.

II. EXPERIMENTAL PROCEDURE

Commercial powders of Fe (99.5% purity, mean particle size 10 μm), La_2O_3 (99.9% purity, mean particle size <2 μm), Nd_2O_3 (99.9% purity, mean particle size <2μm), and Si (99.9% purity, mean particle size <50 μm) were thoroughly mixed in order to obtain a uniform combination of the components, according to the stoichiometric relationship of $La_{1-x}Nd_xFe_{11.3}Si_{1.7}$, where $x = 0.0$, 0.1, 0.3, and 0.5. The mixture was later compacted with excess Ca granules (99.5% purity) under 60 MPa pressure. The pressed pellets were then heated up to 1112 K under Ar atmosphere for the melting of Ca, which activates the reduction process.

After the reduction reaction, the furnace was heated up to 1423 K, allowing the interdiffusion among the metallic elements, La, Nd, Fe, and Si, producing the desired 1:13 phase, with CaO and reminiscent Ca as by-products. A summarized reaction is displayed as follows:

$$\begin{aligned} 1\ \mathrm{RE_2O_3} + 22.6\ \mathrm{Fe} + 3.4\ \mathrm{Si} + 3\mathrm{Ca} \\ \rightarrow 2(\mathrm{REFe_{11.3}Si_{1.7}}) + 3\mathrm{Ca}. \end{aligned} \tag{1}$$

After cooling, the reacted pellet was crushed, and the reaction by-products were later removed in a three-step washing with distilled water, in order to remove soluble CaO and residual Ca, obtaining the desired 1:13 phase.

Aiming at the application in an active magnetic regenerator (AMR), the magnetocaloric compound must have its T_C tuned near AMR operation temperature, so MCE is optimized. Hence, after the washing step, the RD-processed powders were hydrogenated inside a hydrogen-atmosphere furnace at 823 K in order to introduce interstitial H in the 1:13 phase, which expands the crystal lattice and increases its T_C to near-room temperatures.

The thermomagnetic transition was evaluated by means of differential scanning calorimetry (DSC), performed with a TA Instruments 2010 DSC equipment with 5 K/min heating rate, under inert atmosphere.

The microstructures of RD-processed powders were analyzed after the washing step by scanning electron microscopy (SEM) with a FEG-SEM JEOL JSM-6701F in backscattered electron mode (BSE). Chemical composition in each phase was evaluated with the aid of an energy-dispersive X-ray spectroscopy (EDS) module. The amount of the 1:13 phase, as well the presence of undesirable phases, was determined by means of X-ray diffractometry (XRD), followed by a Rietveld refinement of data obtained in an X'Pert diffractometer plus using Cu-K$_\alpha$ radiation (wavelength: 0.15418 nm).

III. RESULTS AND DISCUSSION

The effectiveness of the RD synthesis process was evaluated by XRD. Fig. 1 shows the diffraction pattern for a crushed billet after the RD process with no Nd addition, i.e., before the washing process, in which typical La1(Fe, Si)13 can be observed, as well as the reaction by-products CaO and α-Fe are visible. Any possible reminiscent Ca is considered to oxidize to CaO during XRD sample preparation. Aiming to quantify the phases amounts, Rietveld refinement method was carried out, resulting in 70 wt.% for the 1:13 phase, 20 wt.% for the CaO phase, and about 10 wt.% for reminiscent α-Fe, with an experimental error of 5%, after several batches.

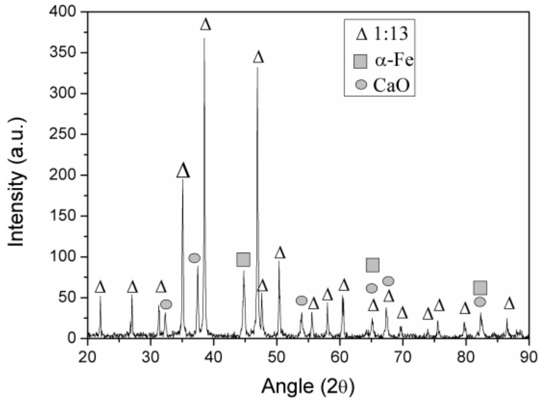

Fig. 1. XRD pattern of the compound obtained by the RD process before the washing step, indicating the presence of the 1:13 Phase, α-Fe and CaO.

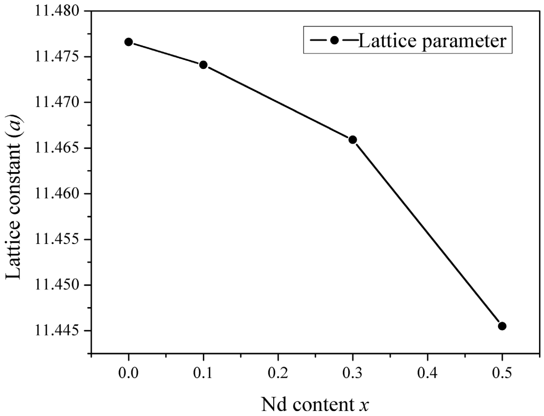

Fig. 2. Variation of the lattice constant (a) as a function of the Nd addition.

In order to evaluate the effectiveness of Nd substitution in the 1:13 phase, the lattice parameter (a) for the different Nd additions ($x = 0.1$, 0.3, and 0.5), were calculated by the Rietveld method, and the results are shown in Fig. 2. The progressive reduction found in the lattice parameter (a) with the increase of Nd addition is a direct evidence of the successful substitution in La sites, this effect being previously demonstrated for conventional casting/heat-treating process.

Phase quantification by Rietveld method was performed on samples after RD with different Nd additions in order to evaluate any influence of this element on RD reaction yields. Fig. 3 shows this quantification, indicating the amounts of alpha-Fe and the 1:13 phase, with the remainder being CaO. Within the experimental error, it can be seen that Nd additions do not significantly change reaction yield, with around 70% of 1:13 phase formed in all different rare-earth proportions. This similarity occurs even though Nd and La oxides present

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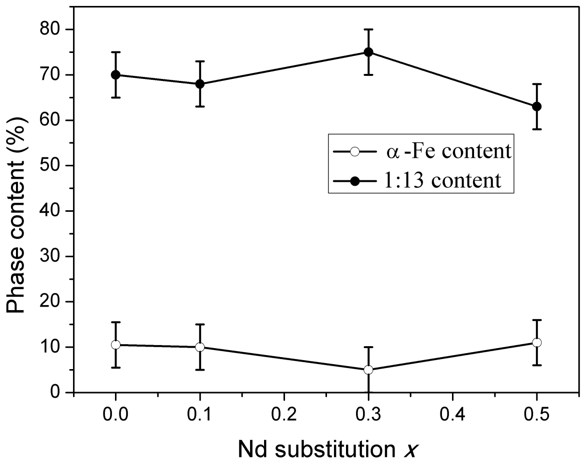

Fig. 3. Evaluation of the reaction yield before washing step by phase quantification for several Nd additions, in which the amount of α-Fe, within the experimental error, remains unaltered.

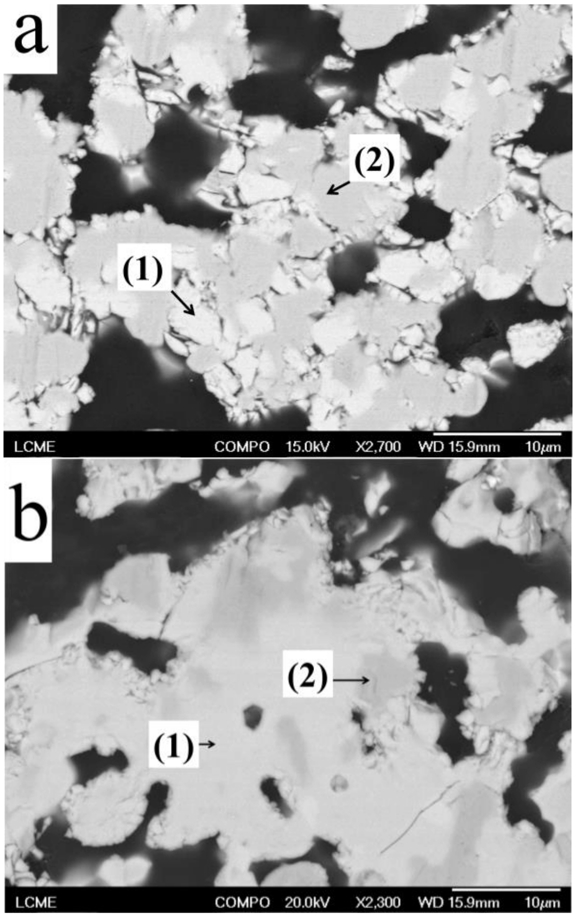

Fig. 4. Morphology and phase distribution along a cross-sectional area of a $La_{1-x}Nd_xFe_{11.3}Si_{1.7}$ RD compound after the washing process, with (a) $x = 0.3$ Nd and (b) $x = 0.5$ Nd, showing the presence of the 1:13 phase (1) mixed with unreacted α-Fe (2).

significant differences in the standard free energy of formation at the reduction temperature (1112 K) [18]. However, the higher stability of CaO in relation to both rare-earth oxides promotes an even conversion of Nd and La oxides to their metallic form, which allows a similar yield in the 1:13 phase formation for all tested Nd:La ratios. Reaction yields are also related to an equivalent diffusivity of Nd and La in Fe, which is in agreement to their chemical and atomic radii similarities.

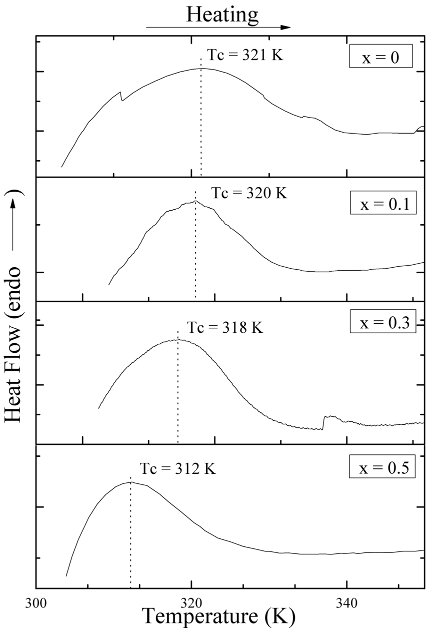

Fig. 5. DSC measurements of $La_{1-x}Nd_xFe_{11.3}Si_{1.7}$ RD compound after the washing process, with $x = 0$, 0.1, 0.3, and 0.5 Nd, with the transition temperature indicated at the maximum height of the peak.

BSE SEM images from the cross section of postprocessed particles after the washing process with two different quantities of Nd ($x = 0.3$ and 0.5) are shown in Fig. 4(a) and (b). The heterogeneous mixture consisted of gray and white regions of around 5 μm observed throughout the particles, showed no significant differences for both Nd additions, with slight variations noticed after the analysis of several particles. The evaluation of phase composition by EDS measurements indicated the gray region as Fe with a small amount of silicon, whereas the white region is composed of the La, Nd, Fe, and Si. No traces of Ca were found in the present phases, an indication that the three-stage washing process is effective. In combination with XRD analysis, it is possible to claim that both phases are α-Fe and 1:13 phase, respectively. In the white region, an increase of EDS peak intensity for Nd in the sample with a higher added amount of this element ($x = 0.5$) was noticed in comparison with $x = 0.3$, which despite being not a quantitative analysis, corroborates the more sensitive evaluation of Nd substitution via XRD.

The resulting morphologies in both compositions show the presence of trapped islands of Fe surrounded by 1:13 phase, which suppresses the contact area with as-reduced rare-earth metals, hence affecting the progress of 1:13 formation. The sintering process that takes place also contributes to form particle clusters, as the ones shown in Fig. 4(a) and (b), that diminishes mass transport mechanisms and also contributes to the reminiscent amount of unreacted α-Fe. In order to circumvent those issues and increase the 1:13 phase reaction yields, further investigations that cover the role of starting particle size and mechanisms to prevent the clustering process are under development.

Fig. 5 show results for DSC measurements that were carried out to observe the magnetic behavior of the 1:13 phase

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with different Nd substitutions, in which endothermic peaks around room-temperature are related to the ferro-paramagnetic transition. This effect can be explained by the change of the magnetic ordering that demands heat absorption from the sample, with the Curie temperature (T_C) being defined at the maximum height of the endothermic peak, which is related to the maximum variation in the heat capacity of the material. For the different Nd additions, a reduction in *Tc* was observed with the increase in the Nd amount, a behavior previously reported in [10], and confirming that Nd atoms are effectively being introduced in the 1:13 phase. The observed Curie temperatures between 310 and 320 K demonstrate the near-room-temperature application potential. It can also be noticed that ferro-paramagnetic transition peaks are narrower in samples with some Nd addition. A smooth transition is expected for the La(Fe, Si)$_{13}$ phase with about 1.7 Si content resulting in a broader peak; however, by the peak profiles shown in Fig. 5, Nd substitutions seem to counteract this effect.

IV. CONCLUSION

The substitution of La by Nd atoms in La1(Fe, Si)13 structure was successfully promoted during the synthesis of this magnetocaloric material by means of the so-called reduction–diffusion process. XRD measurements confirmed the progressive change in lattice parameter related to Nd substitution, in accordance with the starting rare-earth oxide proportions. The change in thermomagnetic behavior promoted by Nd was confirmed by DSC measurements that indicated the expected diminishment on ferro-paramagnetic transition temperature with the increase of Nd substitution. The yield on the 1:13 phase formation was unaffected by the added amount of Nd, this yield being limited mostly by microstructural aspects, such as particle clustering, which decelerates the diffusion process, hence the 1:13 phase formation. According to the presented results, the feasibility of RD process was confirmed for the synthesis of quarternary (La, Nd)1(Fe, Si)13 magnetocaloric compounds with different La:Nd ratios, aiming at the application in magnetic refrigeration.

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REFERENCES

[1] A. Smith, C. R. H. Bahl, R. Bjørk, K. Engelbrecht, K. K. Nielsen, and N. Pryds, "Materials challenges for high performance magnetocaloric refrigeration devices," *Adv. Energy Mater.*, vol. 2, no. 11, pp. 1288–1318, 2012.

[2] K. Löwe *et al.*, "The effect of the thermal decomposition reaction on the mechanical and magnetocaloric properties of La(Fe, Si, Co)$_{13}$," *Acta Mater.*, vol. 60, no. 10, pp. 4268–4276, Jun. 2012.

[3] J. Liu, M. Krautz, K. Skokov, T. G. Woodcock, and O. Gutfleisch, "Systematic study of the microstructure, entropy change and adiabatic temperature change in optimized La–Fe–Si alloys," *Acta Mater.*, vol. 59, no. 9, pp. 3602–3611, May 2011.

[4] A. Fujita and K. Fukamichi, "Control of large magnetocaloric effects in metamagnetic La(Fe$_x$Si$_{1-x}$)$_{13}$ compounds by hydrogenation," *J. Alloys Compounds*, vols. 404–406, pp. 554–558, Dec. 2005.

[5] C. S. Teixeira *et al.*, "Effect of carbon on magnetocaloric effect of LaFe$_{11.6}$Si$_{1.4}$ compounds and on the thermal stability of its hydrides," *J. Appl. Phys.*, vol. 111, no. 7, pp. 11–14, 2012.

[6] M. Balli, M. Rosca, D. Fruchart, and D. Gignoux, "Effect of interstitial nitrogen on magnetism and entropy change of LaFe$_{11.7}$Si$_{1.3}$ compound," *J. Magn. Magn. Mater.*, vol. 321, no. 2, pp. 123–125, 2009.

[7] F.-X. Hu, B.-G. Shen, J.-R. Sun, Z.-H. Cheng, and X.-X. Zhang, "Magnetic entropy change in La(Fe$_{0.98}$Co$_{0.02}$)$_{11.7}$Al$_{1.3}$," *J. Phys. Condens. Matter*, vol. 12, no. 46, pp. L691–L696, 2000.

[8] M. Krautz *et al.*, "Systematic investigation of Mn substituted La(Fe, Si)$_{13}$ alloys and their hydrides for room-temperature magnetocaloric application," *J. Alloys Compounds*, vol. 598, pp. 27–32, Jun. 2014.

[9] D. T. Kim Anh, N. P. Thuy, N. H. Duc, T. T. Nhien, and N. V. Nong, "Magnetism and magnetocaloric effect in La$_{1-y}$Nd$_y$(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ compounds," *J. Magn. Magn. Mater.*, vol. 262, no. 3, pp. 427–431, 2003.

[10] S. Jun, L. Yang-Xian, S. Ji-Rong, and S. Bao-Gen, "Effect of *R* substitution on magnetic properties and magnetocaloric effects of La$_{1-x}R_x$Fe$_{11.5}$Si$_{1.5}$ compounds with R = Ce, Pr and Nd," *Chin. Phys. B*, vol. 18, nos. 1–2, pp. 2058–2062, 2009.

[11] C. He, M.-X. Zhang, Y.-Y. Shao, J.-D. Dong, A.-R. Yan, and J. Liu, "Anomalous microstructure and magnetocaloric properties in off-stoichiometric La–Fe–Si and its hydride," *Chin. Phys. B*, vol. 24, no. 7, pp. 1–5, 2015.

[12] K. Niitsu and R. Kainuma, "Phase equilibria in the Fe–La–Si ternary system," *Intermetallics*, vol. 20, no. 1, pp. 160–169, 2012.

[13] O. Gutfleisch, A. Yan, and K.-H. Müller, "Large magnetocaloric effect in melt-spun LaFe$_{13-x}$Si$_x$," *J. Appl. Phys.*, vol. 97, no. 10, p. 10M305, 2005.

[14] A. Barcza, M. Katter, V. Zellmann, S. Russek, S. Jacobs, and C. Zimm, "Stability and magnetocaloric properties of sintered La(Fe, Mn, Si)$_{13}$H$_z$ alloys," *IEEE Trans. Magn.*, vol. 47, no. 10, pp. 3391–3394, Oct. 2011.

[15] H. N. Bez *et al.*, "Synthesis of room-temperature magnetic refrigerants based on La-Fe-Si by a novel process," *IEEE Trans. Magn.*, vol. 49, no. 8, pp. 4626–4629, Aug. 2013.

[16] C. S. Teixeira *et al.*, "A new feature of the reduction–diffusion process applied for the synthesis of magnetocaloric LaFe$_{13-x}$Si$_x$ compounds," *J. Alloys Compounds*, vol. 541, pp. 84–87, Nov. 2012.

[17] C. S. Teixeira, M. P. Kostow, J. A. Lozano, and P. A. P. Wendhausen, "Room-temperature magnetocaloric effect in LaFe$_{13-x}$Si$_x$ compounds synthesized by calciothermic reduction-diffusion," in *Proc. 4th IIF-IIR Int. Conf. Magn. Refrig. Room Temperature*, Aug. 2010, pp. 73–79.

[18] T. B. Reed, *Free Energy of Formation of Binary Compounds*. Cambridge, MA, USA: MIT Press, 1971.

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