Possible routes for the synthesis of nanowires of intermetallic compounds: The case of CeIn$_3$

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Abstract. In this work, we investigated the role of different parameters in the synthesis of intermetallic nanowires of CeIn$_3$ by the metallic-flux nanonucleation (MFNN) method such as template pore diameter, crystallization temperature, heat treatment temperature, and synthesis time. Depending on the growing parameters, we obtained CeIn$_3$ nanowires (d $\sim$ 350 nm) or CeAlO$_3$ nanotubes. For the nanowires, we observed a suppression of the CeIn$_3$ antiferromagnetic transition from the bulk $T_N \approx$ 10 K to the nanowire system $T_N \approx$ 3 K, which may be associated with the dimensionality affecting the interplay between magnetic exchange interactions, crystalline electrical field, and Kondo effects. We assume that the CeAlO$_3$ nanotubes may result from a reaction with the alumina template and consequent rare-earth oxidation. Our work shows that even it is a great challenge to find the correct growth path of a particular intermetallic compound, the MFNN method can be a promising route to obtain rare-earth based nanowires.

1. Introduction
Correlated intermetallic electron systems exhibit emergent physical phenomena, such as unconventional superconductivity, heavy fermion behavior, complex magnetic ordering, non-Fermi-Liquid behavior, and quantum criticality [1]. These phenomena emerge from the collective behavior of interacting electrons, which is strongly dependent on the system dimensionality [2]. The study of emergent phenomena in reduced dimension systems has been previously reported in different systems [3–6]. Exploring the Fe$_3$Ga$_4$ system, Moura et al. reported a complex change in the phase diagram as a function of the dimensionality [3]. While bulk Fe$_3$Ga$_4$ shows a transition from the ferromagnetic (FM) to antiferromagnetic (AFM) state, Fe$_3$Ga$_4$ nanowires with diameter ($d \approx$ 250 nm) obtained by metallic-flux nanonucleation (MFNN) method [7] exhibit a transition from FM to ferrimagnetic or coexistence of FM and AFM. Previous studies also reported by the synthesis through the MFNN technique and further macroscopic characterization of β-Ga$_2$O$_3$ nanowires with a diameter of 140 nm and length around 3.8 μm [4]. In this case, it was possible to demonstrate the stabilization of a weakly coupled type II superconductor with $T_c \approx$ 6.2 K. Cruz et al. reported the synthesis of oxide-shell-protected Mn$_2$Si$_3$ nanowires with a diameter between 85 and 850 nm by the MFNN method [5]. Electrical characterization showed that nanowires are metallic at low temperatures. Rosa et al. performed a study on the dimensionality effect on the physical properties of the intermetallic compound GdIn$_3$ [6]. Single crystals and nanowires ( $d \approx$ 200 nm and length $l \approx$ 30 μm) of GdIn$_3$ were also grown by the MFNN method. Magnetic susceptibility and specific heat measurements showed a drastic suppression of the AFM order of the bulk system ($T_{\text{AFM}}^{\text{bulk}} = 45$ K) for the $T_{\text{AFM}}^{\text{nanowire}} = 3.8$ K nanowire system. Since Gd$^{3+}$ is an S ion (L = 0), such reduction was associated with changes in the Ruderman–Kittel–Kasuya–Yoshida (RKKY) magnetic interaction.

Due to the flexibility of the Rh$_3$ compound, which allows chemical substitutions in different crystallographic sites, this system represents an excellent opportunity to study the interplay between crystalline electrical field (CEF), Kondo effects, magnetic interactions, and dimensionality [2]. In particular, CeIn$_3$ crystallizes in the simple cubic structure AuCu$_3$ (space group Pm-3m) but has a variety of interesting properties [8]. At ambient pressure, CeIn$_3$ orders antiferromagnetically with $T_N \approx$ 10 K. At pressures of $P \sim$ 25 kbar, the system becomes superconducting with $T_c^{\text{max}} = 0.2$ K. This

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unconventional superconductivity appears around a quantum critical point associated with the destruction of the magnetically ordered state at $T = 0$ K [9]. Here, dimensionality might be another ingredient to understanding the quantum criticality in heavy fermion systems.

In this work, we report the results of growing CeIn$_3$ nanowires using the MFNN method. We systematically investigated the influence of the pore size and template crystallization temperature, heat treatment temperature, and synthesis time on the nanowire growth. In addition, we present the morphological and magnetic characterizations of CeIn$_3$ nanowires and CeAlO$_3$ nanotubes. Our work shows that the MFNN method is a possible but challenging route to obtain rare-earth based nanowires.

2. Experimental
Several attempts to grow CeIn$_3$ were performed using the metallic flux nanonucleation (MFNN) method [7]. This method is a combination of the conventional metal flux growth technique with the addition of a nanometric template for nanowire growth. In this study, we used an Al$_2$O$_3$ template. For the growth of CeIn$_3$ nanowires, a stoichiometry relation of 1 Ce:10 In was used with Al$_2$O$_3$ membranes with pore sizes equal or smaller than $(155 \pm 25)$ nm. The crucible was covered by quartz wool and sealed inside an evacuated quartz tube. We explored the influence of the pore size, membrane crystallization temperature ($T_{\text{crys}} = 900$ or $1150$ °C), maximum heat treatment temperature ($T_{\text{max}} = 850, 950, 1100, 1150, 1200$ °C) and synthesis time (2, 8, 12, 24, 48 h) on the nanowire growth. After the heat treatment, the excess In flux was centrifuged. Both the membrane and the CeIn$_3$ crystals were mechanically removed from the crucible.

The morphology and energy dispersion X-ray spectrometry (EDS) analysis of the CeAlO$_3$ nanotubes were investigated at an FEI Nova NanoLab 200 Dual Beam system (FIB/SEM). The images of the nanowires and their EDS composition mappings were performed at an FEI Inspect F50 microscope. X-ray diffraction measurements of nanotubes and templates were performed at the Brazilian Synchrotron Light Laboratory (LNLS). Magnetization measurements were performed using a commercial magnetometer.

3. Results and discussion

3.1. Morphology and Composition.
We observed nanowires wherein $T_{\text{crys}} = 900$ °C and $T_{\text{max}} = 1100$ °C. Figure 1(a) shows the Scanning Electron Microscopy (SEM) image of an isolated nanowire with a diameter of $(346 \pm 8)$ nm. As shown in Figures 1 (b) and (c), EDS maps confirm that both Ce and In are present at In K$_{\alpha}$ (Figure 1(b)) and for Ce L$_{\alpha}$ (Figure 1(c)) energies, which indicates the formation of CeIn$_3$ nanowires.

![Figure 1](image-url)  
(a) SEM image of the CeIn$_3$ nanowire. EDS composition mapping related to (b) In K$_{\alpha}$ and (c) Ce L$_{\alpha}$ energies.

Several growths were performed with a mean pore diameter equal to or smaller than $(155 \pm 25)$ nm. For each attempt, we varied the $T_{\text{max}}$ (850, 950, 1100, 1150, 1200 °C) or the synthesis time (2, 8, 24, 48 h). Regardless of the chosen parameters, all attempts performed for these templates yielded a presence of nanotubes, as evidenced by the SEM image shown in Figures 2 (a,b). The exception was a growth performed at $T_{\text{max}} = 850$ °C with $T_{\text{crys}} = 900$ °C, for which In nanowires were obtained inside the pores.
Figure 2 (c) shows the point EDS spectrum of a nanotube. We observe the presence of only Ce, Al, and O, which is not consistent with the targeted CeIn$_3$ phase. Figure 2d shows the X-ray diffraction patterns of an alumina template with nanotubes as well as an empty Al$_2$O$_3$ membrane. The orange squares and blue triangles correspond to the indexation from the Inorganic Crystal Structure Database (ICSD no. 72558 and 171679) for the CeAlO$_3$ and In phases, respectively. Both XRD patterns shown in Fig 2d are consistent with the alumina phase. In the case of the template with nanotubes, we also identified peaks consistent with the In and with the tetragonal phase of CeAlO$_3$ (space group: $P4/mmm$) with lattice parameters $a = b = 3.767$ Å and $c = 3.797$ Å [10]. Therefore, XRD measurements and EDS analyses indicate that the nanotubes present the CeAlO$_3$ phase.

The formation of CeAlO$_3$ nanotubes is possibly associated with the chemical composition of the Al$_2$O$_3$ templates. Previous results suggest that Al$_2$O$_3$ templates with a “honeycomb” geometry, i.e., hexagonally ordered circular pores, have a duplex structure of pore walls in terms of chemical composition, an acid-anion contaminated outer oxide layer next to the pores with a relatively pure inner wall oxide [11,12]. In this perspective, the formation of nanotubes may occur due to the reactivity of the Ce$^{3+}$ ions with the relatively pure oxide wall. Exploring further routes by changing the chemical composition of the template could be a promising path to be explored.

**Table 1** Fitted parameters for both bulk and nanowire CeIn$_3$ systems of a Curie–Weiss law plus a temperature-independent term, $\chi(T) = \chi_0 + C/(T - \theta_{CW})$.

| System   | $\theta_{CW}$ (K) | $\chi_0$ (emu/mol.Oe) | $\mu_{eff}$ (µB) |
|----------|------------------|-----------------------|------------------|
| Bulk     | -55              | 7.4 x 10$^{-4}$       | 2.6              |
| Nanowire | -57              | 8.4 x 10$^{-4}$       | 2.1              |
Figure 3b shows the dependence of susceptibility as a function of temperature measured at 10 kOe for CeAlO$_3$ nanotubes grown at different temperatures and synthesis time. The curves show no phase transition, exhibiting a paramagnetic behavior throughout the studied temperature range.

**Figure 3.** Temperature dependence of magnetic susceptibility: (a) for CeIn$_3$ bulk and nanowire, evidencing the Néel temperature; (b) for the Al$_2$O$_3$ template (A81) and CeAlO$_3$ nanotubes grown at different synthesis temperatures.

4. Conclusions

In this work, we explored the routes for synthesizing intermetallic nanowires of CeIn$_3$ via the MFNN method. CeIn$_3$ nanowires were successfully obtained in only one batch with an average diameter of (346 ± 8) nm. Suppression of the AFM transition from ($T_{N}^{\text{bulk}} = 10$ K) to ($T_{N}^{\text{nano}} = 3$ K) was observed in the nanowires. This reduction is possibly associated with the dimensionality affecting the interplay between the RKKY exchange interaction, CEF, and Kondo effects. For several other attempts, the presence of CeAlO$_3$ nanotubes was observed. The MFNN method is a promising but challenging alternative for the fabrication of nanowires of intermetallic systems.

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