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Corrigendum: Methodology and search for superconductivity in the La–Si–C system

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The correct figure 4(c) is presented below. This correction in the abscissa axis does not affect any other results or conclusions of the paper. We gratefully acknowledge Professor I Felner for pointing out this correction.

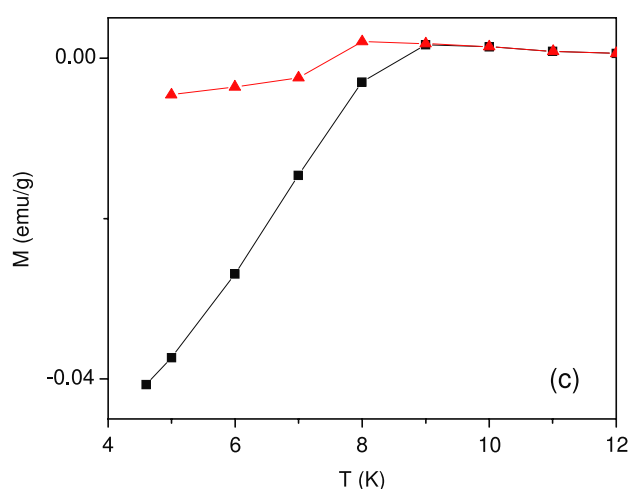


Figure 4. (c) ZFC (—■—) and FC (—▲—) magnetization curves at 100 Oe for sample 3.

Methodology and search for superconductivity in the La–Si–C system

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Abstract

In this paper we describe a methodology for the search for new superconducting materials. This consists of a parallel synthesis of a highly inhomogeneous alloy which covers large areas of the metallurgical phase diagram combined with a fast, microwave-based method which allows non-superconducting portions of the sample to be discarded. Once an inhomogeneous sample containing a minority phase superconductor is identified, we revert to well-known thorough identification methods which include standard physical and structural methods. We show how a systematic structural study helps in avoiding misidentification of new superconducting materials when there are indications from other methods of new discoveries. These ideas are applied to the La–Si–C system which exhibits promising normal state properties which are sometimes correlated with superconductivity. Although this system shows indications for the presence of a new superconducting compound, the careful analysis described here shows that the superconductivity in this system can be attributed to intermediate binary and single phases of the system.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The search for materials with novel properties, new superconductors in particular, is a difficult and sometimes tedious task. It is difficult because a deliberate search for new superconducting materials in a particular system is rarely successful. As a consequence, the discovery of these new materials has been mostly accidental since the discovery of the phenomenon [1–6]. Moreover this is a tedious task because the systems under study are usually materials consisting of several elements with complex phase diagrams. The interesting novel superconducting properties generally occur in a very

narrow phase diagram region where superconducting and non-superconducting phases are likely to coexist. In some ways, the search for new materials is akin to the search for a ‘needle in a haystack’ in which most of the material is ‘irrelevant’.

Based on the past history of discoveries in superconductivity clearly some novel unconventional ideas are needed. Our method consists of a fast process for discarding most of the (‘uninteresting’) non-superconducting part of a multinary phase diagram. This is done by combining a parallel method for the preparation of highly inhomogeneous samples (‘phase spread alloy’) together with a fast, sensitive screening using magnetic field modulated microwave spectroscopy (MFMMS). Once a sample containing a minority superconducting phase is identified, comprehensive and quantitative structural, transport

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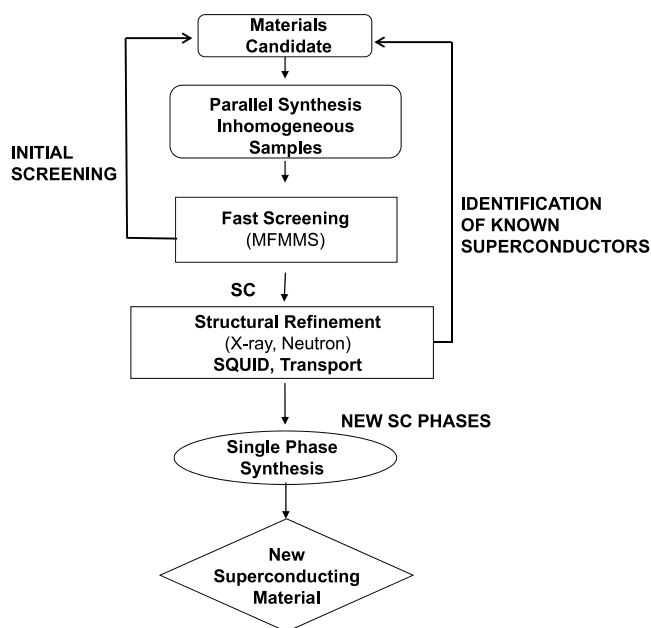


Figure 1. Block diagram of the methodology described here.

and magnetic methods are applied to identify the phase responsible for the superconductivity.

Figure 1 shows a block diagram of the methodology we describe here. The parallel synthesis and fast screening method indicated in the diagram allows large non-superconducting areas of the phase diagram to be discarded. The samples that pass the initial screening stage are then subjected to detailed (albeit slow) magnetic, transport and structural studies to rule out known superconductors. This allows for a rational search among the many possible candidates. In spite of this, the number of possible candidates is enormous and therefore additional restrictions must be used.

The initial starting point of candidate systems necessarily needs some intuitive, theoretical or past-experience-based selection. High temperature superconducting phases (for instance in cuprates) often lurk near other phase boundaries, such as metal–insulator and/or antiferromagnetic phase transitions [7, 8]. They are highly anisotropic, consisting of low dimensional structures which are doped by charges from other portions of the structure. Mixed valency and charge disproportionation seem to be in many cases coincidental with high temperature superconductivity. Usually interesting materials are embedded in multiphase samples where only a small portion is responsible for the superconductivity. In fact the original discovery of high temperature superconductivity in cuprates, for instance, was found in multiphase compounds [4]. This is why an approach intentionally targeting inhomogeneous samples may increase the possibilities of finding new superconducting phases as advocated here.

1.1. Description of the experimental methodology

As an initial step our screening method uses a highly sensitive technique since usually the superconducting phases are only small fractions of the whole sample, as described

above. Conventional superconducting quantum interference device (SQUID) magnetometry is sensitive; however, it is tedious and slow, whereas transport measurements are only useful if a superconducting percolation path is present in the sample. On the other hand, magnetic field modulated microwave spectroscopy (MFMMMS) [9–11] is very sensitive and allows detection of minuscule superconducting regions more quickly and more sensitively than conventional methods, which is particularly useful for highly inhomogeneous systems. Therefore, MFMMMS provides the first screening step and allows large parts of the phase diagram which are not superconducting to be discarded.

Once an inhomogeneous sample containing a minority superconducting phase is found, it is necessary to identify the phase responsible for the superconductivity. This is usually done using a battery of tests including nanoscaled structural, chemical, physical and optical measurements. As a first and powerful approach structural refinement techniques allow identification of the various compounds present in the multiphase sample. This allows not only the pinpointing of and characterizing of new phases but also the identification of impurity phases, which may ultimately be responsible for the observed superconducting properties.

X-ray powder diffraction (XRD) is a well-known structural characterization method for materials, which provides phase and structural information by indexing observed peaks, and fitting the measured intensities with model calculations. In particular, the very successful Rietveld refinement technique uses a least squares fitting approach to obtain a good match of multiphase models with measured data [12]. Laboratory-based powder XRD data provide reasonably good results, although data collected at a synchrotron radiation sources provide a higher flux and a tunable wavelength. Because data obtained at synchrotrons have smaller background contributions, larger signal to noise ratio and better instrumental calibration the results and analysis are usually more reliable. This is somewhat disadvantageous due to the limited beam time available at neutron and synchrotron facilities. However, recent developments, like the mail-in service at beamline 11-BM of the Advanced Photon Source at Argonne National Laboratory [13], enable access to high resolution, synchrotron quality, powder diffraction data in a convenient and timely fashion.

1.2. Materials candidates

In addition to the search methodology described above, it is useful to restrict further the possible candidate systems to decrease the large phase space available. There are a few general guidelines which can be extracted from past experience. It is safe to assume that future discoveries will arise in multi-element compounds, as proven by the recent discovery of superconductivity in the pnictides [6], although even binary alloys (such as magnesium diboride) [3] can go unnoticed for a long time. In most cases, high temperature superconductors contain light elements (such as B, C, N, O, F, S and Cl). Moreover, charge separation among substructures in the material appears, so that both

ionic and metallic/covalent bondings exist side by side, as for example in layered compounds. The proximity to insulating phases (magnetic or charge-ordered) has been also observed in several compounds [7, 8]. Thus as a first approach it is useful to restrict the search to compounds which are multi-element, anisotropic, layered, contain light elements and with some collective order (such as antiferromagnetism) in close proximity. Satisfying simultaneously all the above-mentioned conditions is nontrivial and therefore it may be useful to start from compounds which only partially satisfy them. Moreover, it is worth mentioning that some superconducting systems such as the A15 compounds do not meet the general conditions outlined above. These conditions should be taken as a starting point in order to narrow the initial search. However, taking them as strict rules could hinder the search for many potential new superconductors.

1.3. The La–Si–C system

In accordance with the above-mentioned guidelines here we searched for the presence of superconductivity in the La–Si–C system. This system has some of the common features that appear in superconducting materials. It is a multi-element compound and includes the presence of a light element, in this case C. One of the binary phases, La₅Si₃, has a tetragonal layered structure. In addition, a closely related Nb–Si system presents superconducting behavior when it is doped with B [14].

In the binary La–Si system there are five intermetallic phases: La₅Si₃, La₅Si₄, La₃Si₂, LaSi₂ and LaSi [15]. Among these superconductivity is found in LaSi₂ with α -ThSi₂ crystal structure and a T_C of 2.3 K [16], La₃Si₂ with a T_C near 2.1 K [17], and La₅Si₃ with a T_C at 1.6 K [18]. It has been recently found that under high pressure–high temperature synthesis it is possible to stabilize superconducting LaSi₅ and LaSi₁₀ with T_C of 11.5 K and 6.7 K respectively [19]. The crystal structure of the rare earth silicides of general formula Re₅Si₃ is Cr₅B₃- tetragonal type for the La to Nd group and Mn₅Si₃- hexagonal type for Sm to Lu. Based on earlier expectations C may serve as the light-element dopant and perhaps help to stabilize a hexagonal La₅Si₃ phase as reported previously in Nd₅Si₃, where the addition of C or B stabilized the hexagonal phase [20, 21].

2. Experiment

2.1. Synthesis

Four different polycrystalline, multiphase samples were prepared by arc-melting the constituents on a water-cooled copper hearth under purified argon atmosphere. High purity La (99.95%), Si (99.9995%), and graphite chips (99.9995%) were used to prepare samples with the following nominal compositions: La₃Si₂ (sample 1), La₅Si₃C (sample 2), La_{5.5}Si₃C (sample 3), and La₅Si₃ (sample 4). The samples were turned and remelted four times to ensure homogeneity. The total weight loss after arc-melting was less than 0.3%. Then the samples were wrapped in tantalum foil and sealed in evacuated quartz tubes for further annealing. Samples 1 and

2 were annealed at 1100 °C for three days and then subjected to rapid quenching in liquid nitrogen. Samples 3 and 4 were annealed at 600 °C for three days and then cooled to room temperature over several hours.

2.2. X-ray powder diffraction (XRD)

The synthesized metallic pellets were ground into a fine powder using an agate mortar and pestle to avoid preferred orientation which may produce misleading diffraction patterns. XRD was initially performed in an in-house Bruker D8 Discovery rotating x-ray diffractometer with Cu K α radiation. High resolution synchrotron powder diffraction data were collected using beamline 11-BM at the Advanced Photon Source (APS) at Argonne National Laboratory, using a wavelength of 0.413 52 Å. Discrete detectors covering an angular range from -6° to 16° 2θ were scanned over a 34° 2θ range, with data points collected every 0.001° 2θ and a scan speed of 0.01° s⁻¹ [13, 22, 23]. For the Rietveld refinement we used EXPGUI software [24], a graphical interface for the GSAS package [25].

2.3. Magnetic field modulated microwave spectroscopy (MFMMS)

MFMMS is based on a measurement of temperature dependent phase sensitive microwave absorption while the sample is subjected to an AC modulated magnetic field. The AC field modulation together with phase sensitive detection produces a peak across the superconducting transition [11]. The superconducting onset temperature is correlated with the temperature at which the MFMMS signal falls below the background noise level. We used a Bruker EleXsys EPR spectrometer operating at a frequency of 9.2 GHz with the sample placed in the center of a cylindrical TE₀₁₁ cavity. The spectrometer was operated in a non-conventional mode where the microwave absorption signal was measured as a function of temperature. In the series of experiments described here a 12 Oe external DC magnetic field was applied and modulated at 100 KHz, with a peak-to-peak amplitude of 10 Oe, while the temperature was quickly ramped from 5 to 12 K.

To check the sensitivity of our system we showed that we could detect 3×10^{-11} cm³ superconducting volumes of Nb dots prepared by electron beam lithography on a Si substrate. In a whole different series of earlier experiments and materials systems, we have shown that this method is able to detect as little as 10^{-11} cm³ of a superconducting material embedded in an otherwise non-superconducting matrix [26, 27].

Moreover, this method is also much faster (sometimes by as much as a factor of ~ 100) and more efficient than SQUID magnetometry⁹. Using a SQUID magnetometer, after the temperature is stabilized (typically 30 s) the magnetization of the sample is measured several times. On the other hand, MFMMS scans the microwave absorption while the temperature is rapidly ramped. For instance, a measurement

⁹ The MFMMS technique is 80 times faster than a conventional SQUID magnetometer when it is running a zero field cooled–field cooled cycle from 5 to 300 K with 0.1 K steps compared to MFMMS with the same, or even better sensitivity.

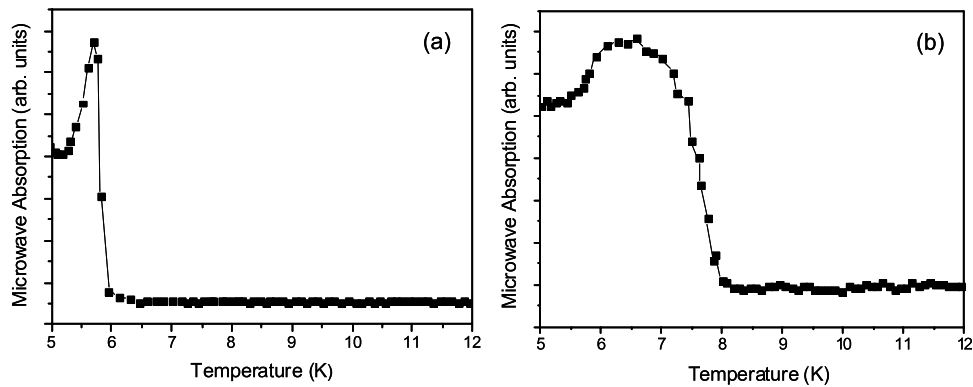


Figure 2. MFMMS response as a function of temperature of (a) sample 2 and (b) sample 3.

from 5 to 12 K takes 8 min with the MFMMS and 41 min with the SQUID magnetometer. Because of this in the MFMMS temperature gradients between the sample and thermometer may occur.

2.4. SQUID

To characterize in detail the superconductivity of the samples that passed the screening, zero field cooled–field cooled (ZFC–FC) magnetizations were measured using SQUID magnetometry. The applied magnetic field was 100 Oe and the temperature was scanned in the 5 to 12 K range.

3. Results and discussion

Following the methodology explained in the introduction, using MFMMS as a fast screening tool, we detected the presence of superconducting phases in the samples containing C (see figure 2). The superconducting transition temperatures are 6.5 K and 8 K for samples 2 and 3 respectively. Since these samples passed the initial screening stage and showed superconducting transitions at temperatures higher than the T_{CS} of the La–Si binary system, they were possible candidates as new superconducting materials. Because of this they were subjected to further detailed characterization.

XRD measurements were performed to obtain phase and structural information on the samples (figure 3). Since most of the intense reflections from the different La–Si phases overlap, it is difficult to distinguish between these phases without careful analysis. For clarification, we have marked in figure 3 some of the reflections arising from La_5Si_3 and La_2C_3 which do not overlap with other diffraction maxima.

Based on an initial analysis, in which peaks corresponding to different La–Si phases were indexed, we can conclude that sample 1 is a mixture of La_3Si_2 and La_5Si_4 phases. Sample 2 is a multiphase compound, with La_3Si_2 as the majority phase; the presence of La_5Si_3 is negligible. Samples 3 and 4 are mixtures of La_5Si_3 , La_3Si_2 and La_5Si_4 . For those two samples, La_5Si_3 is the majority phase.

From the ZFC–FC magnetization curves (figure 4) we conclude that sample 1 is purely diamagnetic, without exhibiting any indications of superconductivity. Samples 2,

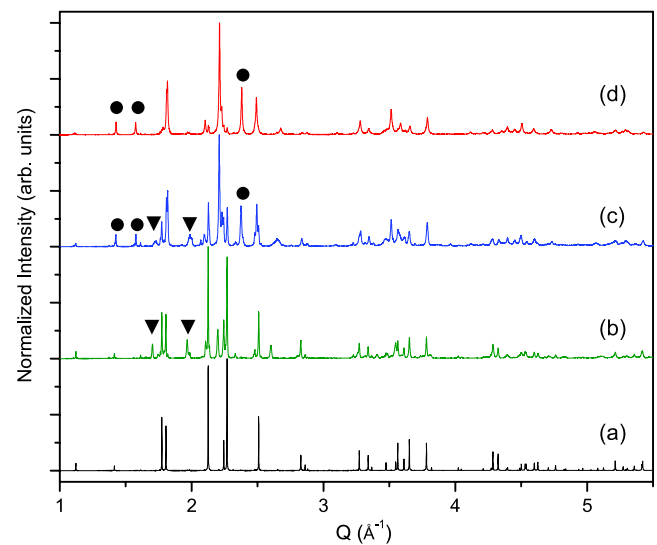


Figure 3. X-ray diffraction patterns of the four different samples: 1 (a), 2 (b), 3 (c) and 4 (d). The ● indicate diffraction maxima from La_5Si_3 and the ▼ indicate those coming from La_2C_3 .

3 and 4 exhibit superconducting transitions at 7 K, 8 K and 6 K respectively. However, the transition in the latter case is different since the ZFC and FC curves split differently from in samples 2 and 3. For samples 2 and 3 the FC is flat and remains very close to zero until it completely separates from the ZFC, which continues to be flat. On the other hand, sample 4 has a smaller magnetization and the ZFC and FC curves remain close while decreasing initially until they start separating at a lower temperature. This shows that the irreversibility temperature, generally related to melting or depinning effects, is different in these samples [28].

The microwave absorption measurements (figure 2) confirm that the magnetization behavior is due to superconductivity. Slight differences between the T_C measured with SQUID and MFMMS were found in our samples. These differences between T_C depend on the microwave frequency [29] and were ascribed to the coupling of microwave currents to fluxons [30], and weak links present below T_C . In addition, here this may be due to temperature differences between the sample holder and

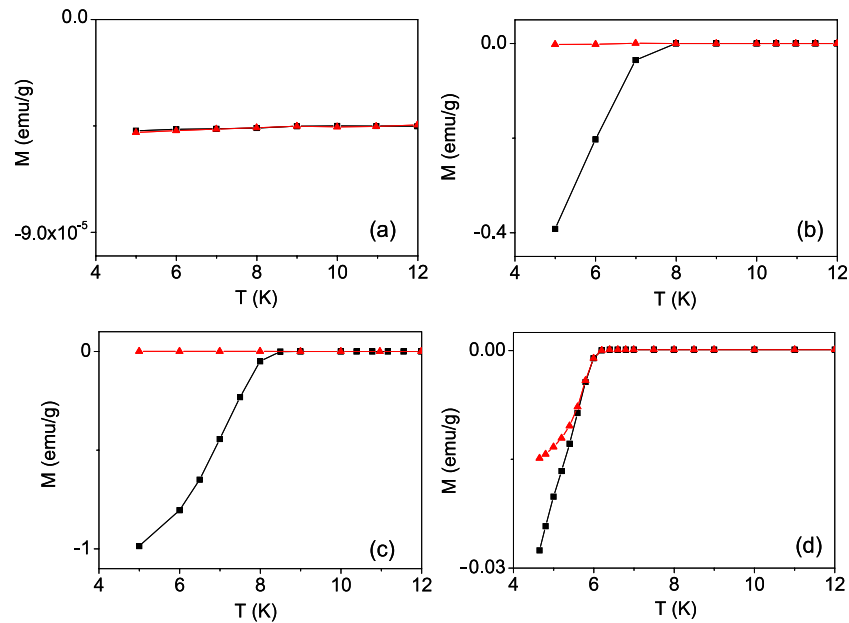


Figure 4. ZFC (—■—) and FC (—▲—) magnetization curves at 100 Oe for samples 1 (a); 2 (b); 3 (c) and 4 (d).

the temperature sensor, which is important for the MFMMS as explained above.

Since the T_C of the binary La–Si family ranges from 1.6 K (La_5Si_3) to 2.3 K (LaSi_2), these results may indicate the discovery of a new superconducting phase. This potential new superconductor, which is produced by doping C into the La–Si system, has a T_C between 7 and 8 K. Another potential superconductor could be ascribed to the 6.1 K transition observed in sample 4. This sample does not contain C and exhibits a different behavior in the superconducting transition (figure 4).

To clarify the origin of superconductivity, it is essential to carefully check and investigate the presence of already known superconducting compounds which may be present as impurities or intermediate phases. To obtain quantitative results from x-ray synchrotron data we performed Rietveld refinement. Figure 5 shows the observed and calculated XRD profiles for one of the samples (number 3). The ‘chi squared’ (χ^2), ‘weighted profile R -factor’ (R_{wp}) and phase weight fractions of the significant compounds found are given in table 1.

All possible phases containing La, Si and C as single elements, their binary and ternary combinations and possible oxides formed during the syntheses were taken into account in the refinement process. The last issue is particularly important for the case of La, an element that quickly oxidizes. Only minute fractions of La_2O_3 were found in the x-ray diffraction patterns of samples 2 and 3.

The values of χ^2 displayed in table 1 are far from the ideal value of 1, especially for sample 2, which is usually the case for high precision data [31]. Rietveld refinement using the data acquired in our laboratory-based diffractometer, gives χ^2 very close to 1. This is partially due to the lower resolution of the lab-based data, and also reflects the larger fitted background contribution needed for a lower intensity

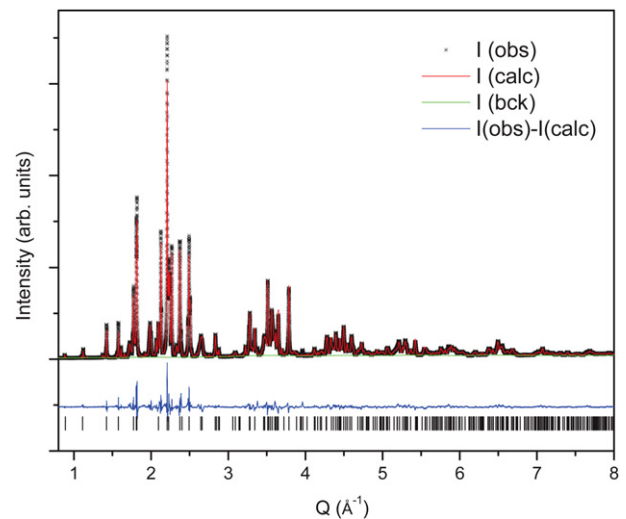


Figure 5. Rietveld refinement profile of the x-ray powder diffraction data for sample 3. Tick marks indicate reflections coming from the majority phase La_5Si_3 .

source. Also, the random error in each synchrotron acquired data point is small; therefore small disagreements in the fit become more significant when comparing experimental and calculated patterns. Even with these drawbacks, it is preferable to work with the synchrotron data, because the resolution is better and Rietveld refinement results are more reliable since the instrument is carefully calibrated.

From the analysis described above we found clear indication for the presence of the phases displayed in table 2. There is no evidence of La_5Si_3 in Cr_5B_3 -prototype hexagonal structure, $P63/mcm(193)$, in any of the samples. This hexagonal phase may be stabilized in the Nd_5Si_3 system when it is doped with C and B [20, 21] and in the superconducting ($T_C = 7.8$ K) Nb_5Si_3 system doped with B [14].

Table 1. Refinement factors χ^2 , R_{wp} , weight fraction of each phase and T_C for the different samples.

	Sample (intended composition)			
	1 (La ₃ Si ₂)	2 (La ₅ Si ₃ C)	3 (La _{5.5} Si ₃ C)	4 (La ₅ Si ₃)
χ^2	11.62	28.31	12.16	11.10
R_{wp}	0.1151	0.1495	0.0984	0.0937
Weight fractions	La ₅ Si ₃	—	97.95%	99.73%
	La ₃ Si ₂	95.70%	63.26%	0.89%
	La ₅ Si ₄	4.30%	13.20%	0.48%
	La ₂ C ₃	—	23.50%	0.67%
	La β	—	—	—
T_C (K)	—	7	8	6

Table 2. Crystal structures of the different phases unidentified in the samples.

	Phase			
	La ₅ Si ₃	La ₃ Si ₂	La ₅ Si ₄	La ₂ C ₃
Structure type	Tetragonal	Tetragonal	Tetragonal	Cubic
PDF number	01-070-8888	19-660	01-070-8805	01-082-0622
Space group	<i>I4/mcm</i> (140)	<i>P4/mbm</i> (127)	<i>P41212</i> (92)	<i>I-43d</i> (220)
Unit cell parameters (Å)	<i>a</i>	7.976	7.87	8.0467
	<i>b</i>	7.976	7.87	8.0467
	<i>c</i>	14.107	4.50	15.4476

The results from sample 2 (table 1) indicate that the superconductivity is not caused by the presence of the layered La₅Si₃ phase since even the sample composed mainly of La₃Si₂ shows a T_C of 7 K. Sample 1, without C, does not display any signs of superconductivity. Therefore the T_C s in samples 2 and 3 (7 and 8 K) are related to the presence of C. Sample 4, a sample without C as a starting material, also shows traces of superconductivity. Nevertheless, the T_C of 6.1 K, the shape of the transition as well the values of the magnetization (figure 4) are different from the other superconducting samples. So the origin of this transition temperature could be different from samples 2 and 3. The T_C around 6 K is very close to the La β transition temperature and including it in the Rietveld refinement improves the fit. Therefore the superconductivity in sample 4 is ascribed to the La β phase.

For samples 2 and 3 containing C as a starting material an improved refinement is obtained if the La₂C₃ compound is included as one of the phases. The superconductivity of this compound is strongly dependent on the C deficiency, with T_C ranging from 5.5 to 13 K for compositions La₂C_{3-x}, with $x = 0.27$ and 0 respectively [32]. The maxima in the diffraction patterns at Q values of 1.71 and 1.97 Å⁻¹, marked with the ▼ symbols in figure 3, could not be attributed to any phases of the La–Si system. The values are in the same positions as the allowed reflections coming from La₂C₃ assuming a lattice expansion of 2.5%. Also the diffraction pattern presents maxima at La₂C₃ angle reflections, assuming a lattice expansion of 1.3%.

Rietveld refinement implies that the concentrations of the La₃C₂ phase are 23.5% and 0.67% for samples 2 and 3, respectively (table 1). From SQUID magnetometry, at 5 K and 100 Oe the shielding moments are -0.4 emu g⁻¹ and -0.04 emu g⁻¹ for samples 2 and 3, respectively (figures 4(b) and (c)). These values of the magnetization correspond to

shielding fractions of 28% and 2.8% (assuming a density of 5.7 g cm⁻³). These shielding fraction values are close to the phase concentration percentages, indicating that the superconductivity is related to the presence of the La₃C₂ phase. The small differences in these values could be ascribed to the inhomogeneous distribution of the La₂C₃ phase in the samples.

Thus the occurrence of superconductivity in samples 2 and 3 is ascribed to the presence of La₂C₃, which is further supported by the Rietveld refinement and superconducting shielding fraction obtained from SQUID magnetometry. So this superconductivity could neither be ascribed to new crystal structures formed by the addition of C nor to the doping of the layered La₅Si₃ structure with a light element. The different transition temperatures may be related to different La₂C_{3-x} compositions [32] with the larger C deficiency leading to the lower T_C . Assuming that larger Si replace C atoms in La₂C_{3-x}, the T_C variations are consistent with the lattice expansions. Sample 2 presents a lower T_C and a larger lattice expansion, whereas sample 3 has a higher T_C and a smaller lattice expansion.

4. Conclusions

In conclusion, we have described a new approach for the search for new high T_C superconducting materials. We have applied this method to the La–Si–C system, which shows normal state properties similar to high T_C superconductors. Fast screening indicates the presence of possible new superconducting phases. However, a careful structural analysis implies that the superconductivity may be ascribed to the presence of the already known La₂C₃ and La β superconductors. As a general rule, when the T_C of multi-element materials is below or close to the T_C of any of the single elements or partial compounds, the results should be taken with extreme

caution. All checks must be made in order to avoid mistaken conclusions. Although no new superconductivity has been found in the La–Si–C system yet, we identified the origin of the superconductivity using the methodology described above. This shows the power of this method for future searches for new superconducting phases.

Acknowledgments

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