

Influence of Rare-Earth Inclusion on Structure and Properties of Ca/K-1144 IBSC

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Abstract—Among Iron Based superconductors (IBSC), the compounds belonging to the 1144 family are characterized by the $A_1AE_1Fe_4As_4$ chemical composition (A = Alkaline, AE = Alkaline-Earth) and considered stoichiometric. In recent experiments, we obtained 1144 samples characterized by different levels of alkali and alkaline earth metals substitutions and demonstrated how the lattice distortion induced by such variation in the chemical composition plays a fundamental role on critical temperature values. In this work, we investigate the possibility to obtain Ca/K-1144 compounds substituted with Rare-Earth (RE) elements. We produced polycrystalline samples in which RE ions partially replace Ca ions in the 1144 phase. The lattice structure is consistently affected by the substituent element inducing a contraction of the *c*-axis. Multiple substitution of RE and A or AE elements was also attempted, showing that appropriate combinations allow simultaneous inclusion of different elements in the structure. For compounds that include RE elements, the critical temperature of the samples appears to follow to the same trend with respect to the distortion of the crystal lattice induced by A and AE substitutions.

Index Terms—1144 superconductors, iron based superconductors, rare earths, X-ray diffraction.

I. INTRODUCTION

IRON-BASED superconductors, discovered in 2008 [1] have triggered rapid research directed towards both scientific and technological aspects [2]. These compounds are characterized by a ‘layered’ structure in which (Fe) ions are tetrahedrally coordinated by pnictogen (P, As) or chalcogen (S, Se, Te), and between these layers different elements or molecules can be intercalated, thus categorizing IBSCs to different families. The

so called 1144 family was recently discovered and characterized by the following composition ($AE_1A_1Fe_4As_4$) with Alkali and Alkaline Earth metals (AE = Ca, Sr and A = K, Rb, Cs) in 1:1 stoichiometric ratio [3].

Structurally, this family is very similar to the 122 (AE/AFe_2As_2) family. Both have alternating A and AE metals among Fe-As planes. The main difference is that in AE/A-122 structure (*I4/mmm* symmetry group), the A and AE elements share the same crystalline site, because of their similar ionic radii. In the AE/A-1144 structure, the difference in size between the A and AE elements leads them to a rigid, alternating distribution between the Fe-As planes, which in turn leads to an increase in the symmetry represented by the *P4/mmm* space group. Precisely this rigid AE/A ratio fixed at 1 gives the 1144 family a stoichiometric nature and consequently also solid critical temperature values [4]. Conversely, it is known that the critical temperature of AE/A-122 phases is influenced by the different AE/A ratio [4], [5]. In our previous works [6], [7], we investigated whether it was possible to vary the AE/A ratio in 1144, while still maintaining a clean 1144 phase but influencing the superconducting properties as with the 122 family. For this purpose, we performed partial substitutions in the Ca/K-1144 compound (Ca/K = 1) of Ca and K with A and AE metals and showed that such substitutions are possible for ions with similar ionic radius. Furthermore, it was shown that substitutions affect the crystalline cell parameters, producing a narrowing or elongation of the *c*-axis. Finally, we found a dome-shaped relationship between the critical temperature and the *c/a* parameter (the tetragonality parameter was used as representative of the structural variation of substituted compounds), and showed how the lattice distortion induced by this variation in chemical composition plays a key role on the critical temperature values.

In this work, we examine the possibility of using other elements as substituents in the Ca/K-1144 compound besides A and AE metals, such as rare earths (RE), and their possible influence on superconducting properties. Light RE possess in fact ionic radii close to Calcium. This should represent a key factor in preserving the initial lattice structure, as shown in Ca-122 phases, where an opportune substitution has proven possible, with resulting cell distortion dependent on the substituent ionic radius [8], [9]. Considering that in our previous work we showed that it is possible to form a 1144 phase with a partial substitution of K (152 pm) with Sr (132 pm) [6], we have studied substitutions of Ca (114 pm) also with smaller radii RE (e.g., Er 103 pm).

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Adopting a mechanochemically assisted synthesis, variously substituted bulk polycrystalline samples are obtained. The substitutions studied are: single partial substitutions of Ca (114 pm) with La (117.2 pm), Pr (113 pm), Sm (109.8 pm) and Er (103 pm) and multiple partial substitutions of Ca with La and Na (116 pm) and of Ca and K (152 pm) with La and Ba (149 pm) respectively.

The samples synthesized are characterized in terms of crystal structure through X-ray diffraction analysis, and morphology is assessed through scanning electron microscopy (SEM) measurements. The change in the superconducting critical temperature induced by substitutions is assessed by direct current (DC) electrical resistance measurements.

II. EXPERIMENTAL

Materials are synthesized according to the route reported in our previous works [10], [11]. The starting elements are: arsenic powder from Alfa Aesar, 99%, potassium cubes from Alfa Aesar, 99.5%, calcium granules from Sigma Aldrich, 99.5%, iron powder from Alfa Aesar, 99.998%, erbium powder from Alfa, 99%, samarium pieces from ThermoScientific 99.9%, praseodimium cubes from Alfa Aesar 99%, lanthanum granules from Aldrich, 99.9%, Barium rods from Alfa Aesar, 99+% and Na ingots from Alfa Aesar, 99.8%). The milled powders were pressed into disk-shaped pellets (diameter $d \approx 5$ mm, thickness $h \approx 0.5$ –1 mm) by uniaxial pressing and heated inside a sealed steel tube containing an inert crucible for 10 h at 800 °C with a 10 °C min^{-1} heating rate and a 5 °C min^{-1} cooling rate.

All starting compositions were characterized by an excess in the A, AE and As, as can be seen from the nominal starting composition $\text{Ca}:\text{K}:\text{Fe}:\text{As} = 1.27:1.175:3.8:4$, introduced to counterbalance the oxidation of the starting elements [10].

XRD analysis was carried out on the thermally reacted crushed pellets in sealed glass capillaries using a diffractometer equipped with a 120° linear simultaneous detector from INEL–Thermo Fisher Scientific and a monochromatized $\text{Fe } K \alpha_1$ source.

Lattice parameters of the Ca/K-1144 like phases (see the following section for details) were estimated through pseudo-Voigt fitting of the experimental diffraction patterns with the in-built routine of the Match! Software [12], fitting the most intense peaks of each pattern assuming a $P4/mmm$ phase (space group 123) modelled following the work of Iyo et al. [1].

SEM analyses were performed with a Leo 1525 SEM equipped with an Oxford x-act energy dispersive spectroscopy system. DC electrical resistance was measured using a standard four contacts method placing the contacts on the edges of the disk-shaped pellets. To assess the critical temperature, the transition onset value was estimated as the point of deviation from the linear extrapolation of the normal state resistance. An experimental uncertainty of $\pm 0.5\text{K}$ was evaluated on the basis of statistical analyses on nominally identical samples.

III. RESULT AND DISCUSSION

The XRD patterns of the different Ca/K samples variously substituted with RE and AE and/or A are shown in Figs. 1, 2

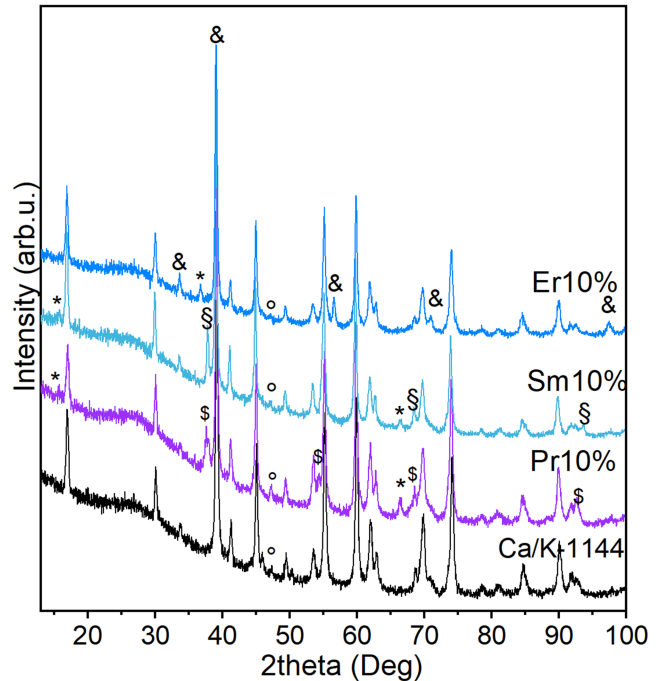


Fig. 1. XRD patterns of different substituted compounds in comparison with the pattern of unsubstituted Ca/K-1144 compound; &, \$, *, * and ° mark ErAs, SmAs, PrAs, K-122 and CaO.

and 3. In more detail, Fig. 1 shows a series of characteristic diffraction patterns of the three samples, in each of which 10 percent Ca was replaced with 10 percent Pr, Sm and Er, and of the unsubstituted Ca/K-1144 sample to highlight any changes induced by the substitutions.

All samples show major peaks attributable to a Ca/K-1144-like phase and minor peaks belonging to secondary phases such as Rare-Earth arsenides, calcium oxide and K-122. More detailed analysis of the main peaks of the 1144 phase of the substituted samples revealed no significant structural changes compared to the unsubstituted Ca/K-1144 compound. From these results, it appears that the elements that were supposed to replace calcium in the Ca/K-1144 structure were eventually present as RE arsenides.

Fig. 2 shows the diffraction patterns of the series of La substitutions in which Ca was replaced with 5%, 10% and 20% La. In all substituted samples, the presence of major peaks attributable to the Ca/K-1144 phase and minor peaks due to the presence of calcium oxide can be observed.

In the inset it can be seen that La substitution leads to a shift of the diffraction peaks, which suggests that the chemical substitution has occurred and brings with it a consistent structural change compared to the unsubstituted Ca/K compound (for clarity shown in the same graph). In addition, a decrease in the peak (115) intensity is observed in the La20% diffraction profile. The presence of this reflection is important because it is representative of the $P4/mmm$ space group characteristic of phase 1144, while in the $I4/mmm$ space group characteristic of phase 122 this reflection is absent. This reflection can therefore be used as an indicator of a loss of order in the 1144 structure;

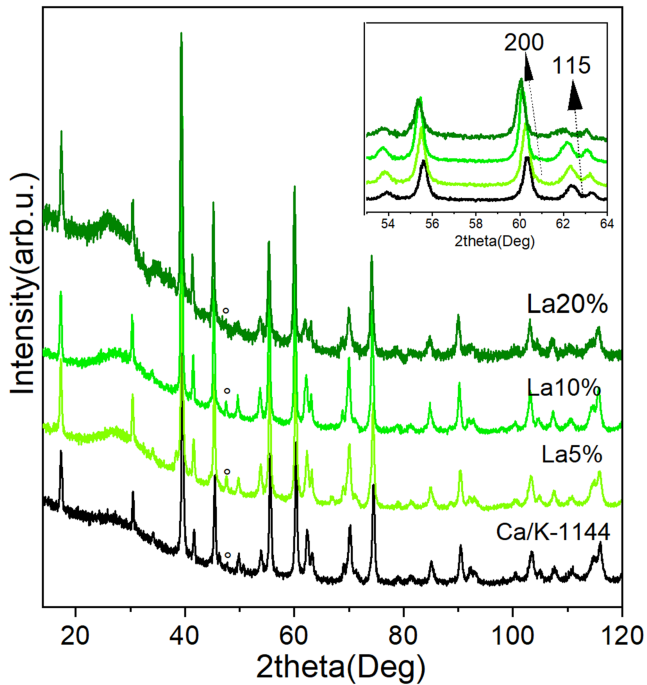


Fig. 2. XRD pattern of the La substituted compounds in comparison with the pattern of unsubstituted Ca/K-1144 compound; ° mark CaO.

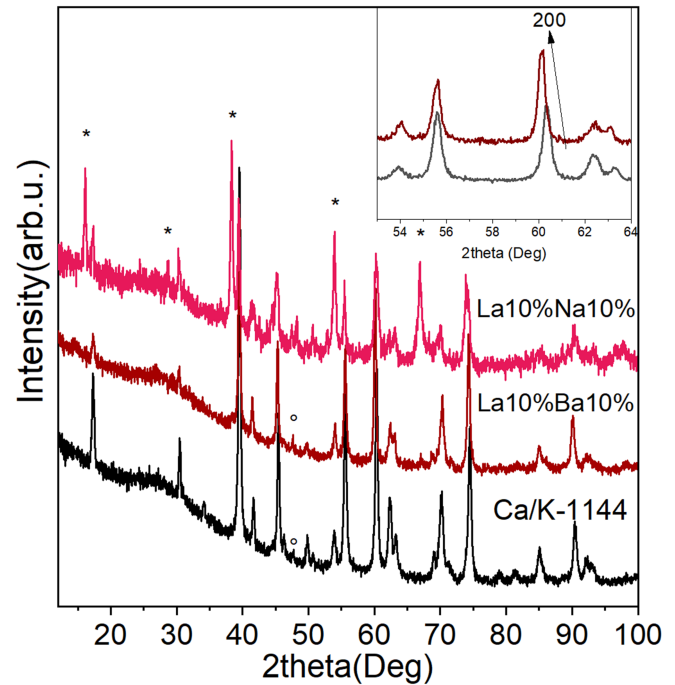


Fig. 3. XRD pattern of the doubly substituted compounds in comparison with the pattern of unsubstituted Ca/K-1144 compound; * and ° mark K-122 and CaO.

in fact, its disappearance in the La20% spectrum suggests that the high degree of substitution leads to disorder in the planes of ions of different sizes (Ca and K) in the Ca/K-1144 structure.

Finally, Fig. 3 shows the patterns of the samples in which double partial substitution was studied. Specifically, in the La10%Na10% sample 20% Ca was replaced with 10%La+10%Na: as can be seen from the pattern such substitution is not successful and gives rise to secondary phases. The La10%Ba10% sample, in which 10% Ca and 10% K were simultaneously replaced with 10% La and 10% Ba, respectively, shows instead that the synthesis was successful as the substitution results in a clean 1144 phase, with a significant structural change from the unsubstituted Ca/K-1144 compound.

The morphology of the La10% sample is shown in Fig. 4 as representative of the substituted compounds. As can be seen from the SEM image, the sample consists of dense aggregates (tens of microns) surrounded by regions of irregular porosity. The aggregates are formed by small crystals, hundreds of nanometers large. No significant difference is observed between the unsubstituted Ca/K-1144 sample (e.g., [6]) and the sample with 10% La substitution.

Another important aspect is the superconducting transition of the different samples, illustrated in Fig. 5. The Sm10% and Er10% are characterized by a T_c onset close to 35 K, showing no significant differences compared to the unsubstituted Ca/K-1144 sample (shown in the same graph for clarity) As for sample Pr10%, its $T_c = 34.2$ K seems to be slightly affected compared to the unsubstituted compound. One may suspect a low solubility level of Pr in the Ca/K-1144 phase, as later discussed in the

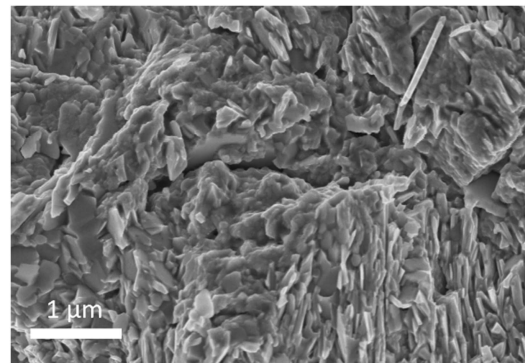


Fig. 4. SEM image of La10% ($\text{Ca}_{0.9}\text{La}_{0.1}\text{KFe}_4\text{As}_4$) sample.

text. Regarding the La series, also reported in Fig. 5, there is a tendency for the critical temperature to decrease as the amount of dopant increases: onset values of 34.7 K, 32.1 K and 29 K where obtained respectively for the 5%, 10% and 20% substituted samples. A similar tendency was noted for the A and AE substitutions in our previous work. The La10%Ba10% sample also shows a change from the unsubstituted compound, with an observed T_c onset of 20.4 K.

Next, we plotted the T_c values as a function of the c/a parameter of samples La5%, La10%, La20% and Ba10%La10% together with other partially substituted $\text{CaKFe}_4\text{As}_4$. The points fall on the left side of the graph, corresponding to the contraction of the c -axis, as also observed when replacing K with Ba and Sr. The trend of the resulting points follows and falls within the bell-shaped pattern shown in Fig. 6 and described in our previous work on substitutions with A and/or AE [7]. Furthermore, also

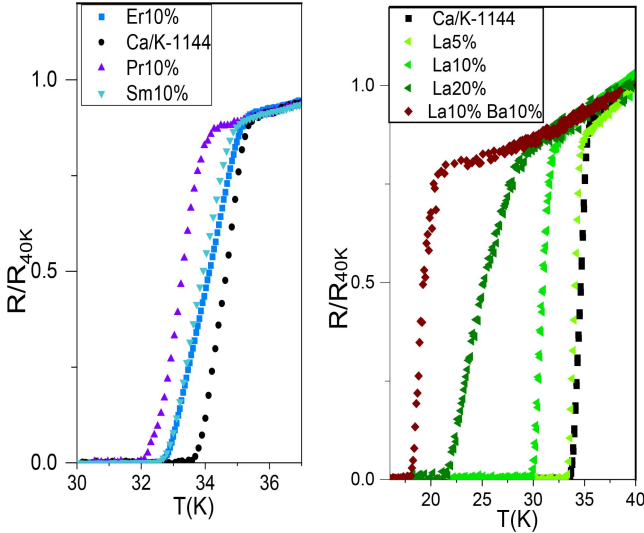


Fig. 5. Superconducting transition of the different samples.

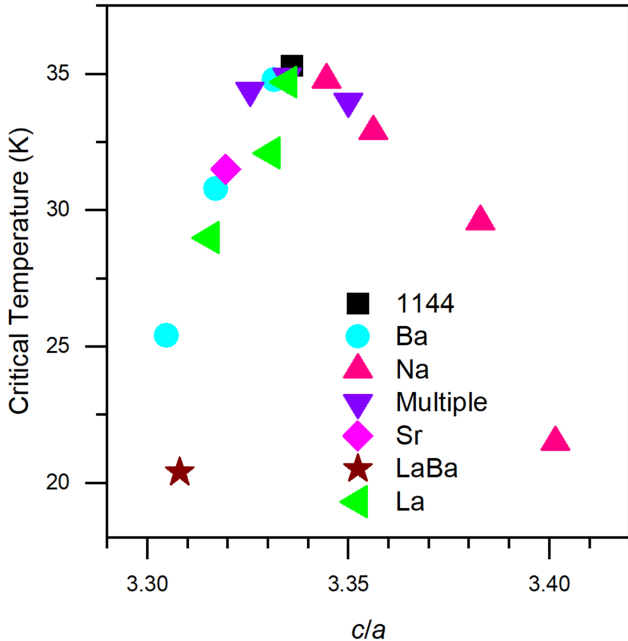


Fig. 6. Critical temperature as a function of the lattice tetragonality ratio for the different substitutions. The curve is taken from [7] and updated with points measured in this work. The series of “multiple” refers to partial double substitutions at different concentrations of Ca with Na and K with Ba i.e., Na5%Ba10%, Na10%Ba10% and Na10%Ba20%.

for the reported samples, we can exclude a primary role of charge doping on the T_c value, as samples with the same iron valence value such as e.g., La20% and La10%Ba10% show significantly different T_c values.

To understand why among all the REs tested only La seems to fit well into the Ca/K-1144 structure as a Ca substituent, it may be useful to compare with previous literature regarding Ca-122 phases. Previous studies on Ca-122 show that REs can enter the

lattice by substituting Ca ions. The introduction of RE into the 122 lattice creates a distortion, specifically a contraction of the c -axis [8], [9]. This lattice distortion is more pronounced when the difference between the values of the ionic radii of Ca and the RE substituent increases. Furthermore, in the work of Zhou et al. [8], it was shown that in the Ca-122 there is a negative relation between the distortion caused by substitution with a RE and its solubility limit. For example, La, characterized by the closest ionic radius to Ca, leads to a minor lattice distortion and this seems to be reflected in a higher solubility limit.

It is plausible to assume that a similar mechanism applies for the 1144 family. Experimental evidences here reported show the solubility limit of La in $\text{CaKFe}_4\text{As}_4$ is found to be approximately $x \approx 0.2$, much lower than the solubility limit of La in Ca-122 [8], while Pr, Sm and Er substitution is not clearly incorporated in the $\text{CaKFe}_4\text{As}_4$ phase. For a direct comparison, in the Ca-122 phase the solubility limit of Pr is close to $x \approx 0.2$, while in our work a substitution of 10% led to significant secondary phases segregations, suggesting that in $\text{CaKFe}_4\text{As}_4$ the solubility limit will be much lower. This may suggest that the crystalline structure of 1144 is less flexible to accommodate substituents. We show thus that the substitution of Ca with RE is possible, but that the solubility limits reported for the RE inclusion in Ca/K-1144 phase are lower than the ones observed for the Ca-122 phase.

IV. CONCLUSION

In this work, we studied the substitutions in Ca/K-1144 compounds with RE (La, Pr, Sm and Er) and with RE and A or Ae (Na and La, Ba and La) carried out by mechanochemically assisted synthesis followed by heat treatment.

From XRD analyses, it was observed that La can be used as substituent in Ca/K-1144 compounds, giving rise to a clean phase and to a distortion of the lattice. In these compounds, the substitution caused a consistent change in T_c . No significant effect is seen on the morphology of the La10% sample, representative of the entire series, characterized by the main presence of dense aggregates of small crystals in agreement with that seen for the unsubstituted sample. The other rare earths (RE) tested did not result in a clean Ca/K-1144 crystalline structure and gave rise to the formation of RE arsenides.

Regarding the double substitution with Ba and La, it was observed, again, that this substitution allows to obtain a clean Ca/K-1144 phase with the respective change in T_c value.

Experimental data show that the tendency observed in the trend of critical temperatures as a function of tetragonality ration (c/a) is confirmed with Rare Earths and not only limited to alkali and alkaline earth metals.

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