

# Single-Crystal X-ray Diffraction Study of Doped $\text{CaKFe}_4\text{As}_4$ : Structural Distortions.

A. Duchenko<sup>1,2,3</sup>, A. Angrisani Armenio<sup>3</sup>, L. Barba<sup>4</sup>, Y. Chen<sup>5</sup>, F. Laviano<sup>2</sup>, P. K. Mondal<sup>6</sup>, L. Muzzi<sup>3</sup>, N. Pompeo<sup>1</sup>, T. Tamegai<sup>5</sup>, F. Varsano<sup>7</sup>, A. Masi<sup>3\*</sup>

<sup>1</sup> Università degli Studi RomaTre, Dipartimento di Ingegneria Industriale, Elettronica e Meccanica, Via Vito Volterra, 62, 00146 Roma, Italy;

<sup>2</sup> Department of Applied Science and Technology (DISAT), Politecnico di Torino, Torino, Italy;

<sup>3</sup> ENEA, NUC-FUSEN-COND, Via Enrico Fermi, 45, 00044 Roma, Italy;

<sup>4</sup> CNR – Institute of Crystallography, X-ray Diffraction Beamline at Elettra, Area Science Park, 34149 Basovizza (TS), Italy;

<sup>5</sup> Institute for Solid State Physics, The University of Tokyo, Kashiwa, Chiba 277-8581, Japan;

<sup>6</sup> X-Ray Diffraction Beamline (XRD1), Elettra – Sincrotrone Trieste S.C.p.A., Trieste, Italy; <sup>7</sup>ENEA, C.R. Casaccia, Via Anguillarese, 301, 00123 Roma, Italy.

## INTRODUCTION & AIM

**Iron-based superconductors (IBSs)**, discovered in 2008, are layered materials composed of superconducting FePn (Pn = P, As) or FeCh (Ch = Se, Te) layers separated by spacer layers containing different atoms, elements, or molecular groups. They are classified into structural families such as 11, 111, 1111, 122, and 1144. Their moderate critical temperatures ( $T_c \approx 15\text{--}58\text{ K}$ ), high upper critical fields ( $H_{c2} > 50\text{--}100\text{ T}$ ), and large critical current densities ( $J_c > 10^5\text{--}10^6\text{ A/cm}^2$ ) make them promising candidates for superconducting wires and high-field magnet applications. **Chemical substitution** is a well-established strategy for tuning superconducting properties. Since the discovery of the 1144 family in 2016, understanding the interplay between chemical substitution, structural distortions, and superconductivity has become an important research topic. In our previous work,  $\text{CaKFe}_4\text{As}_4$  was chosen as the parent compound and reference material [1-3].

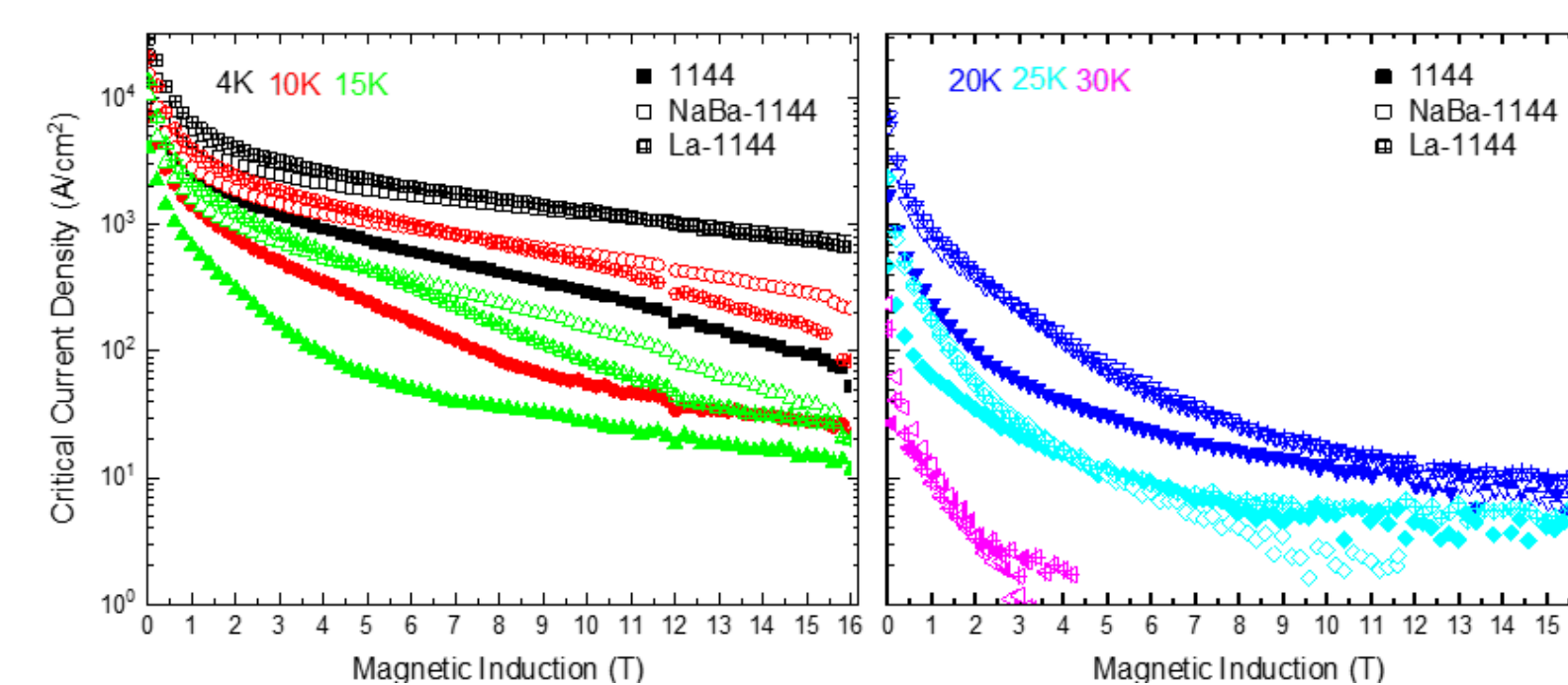
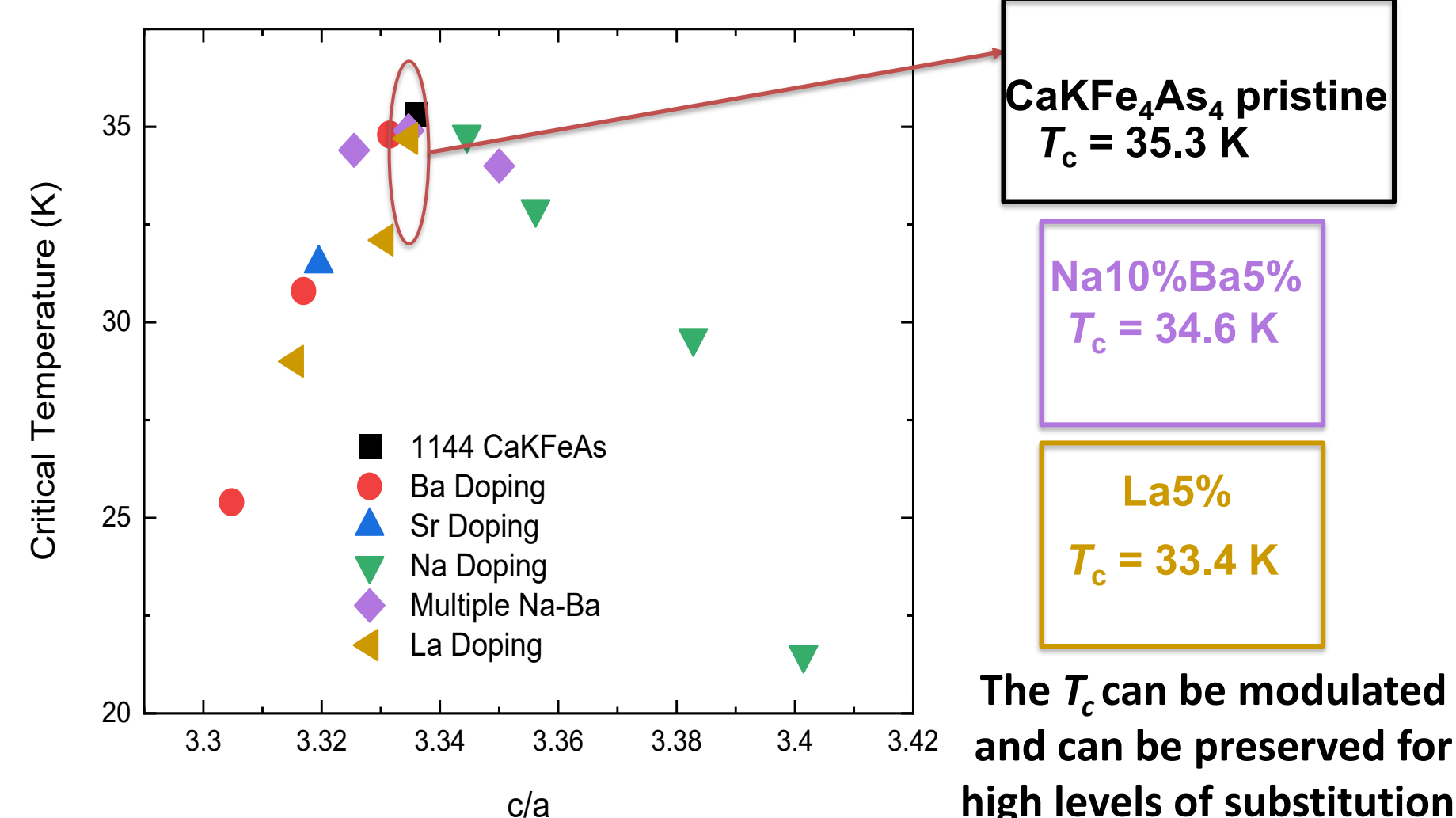
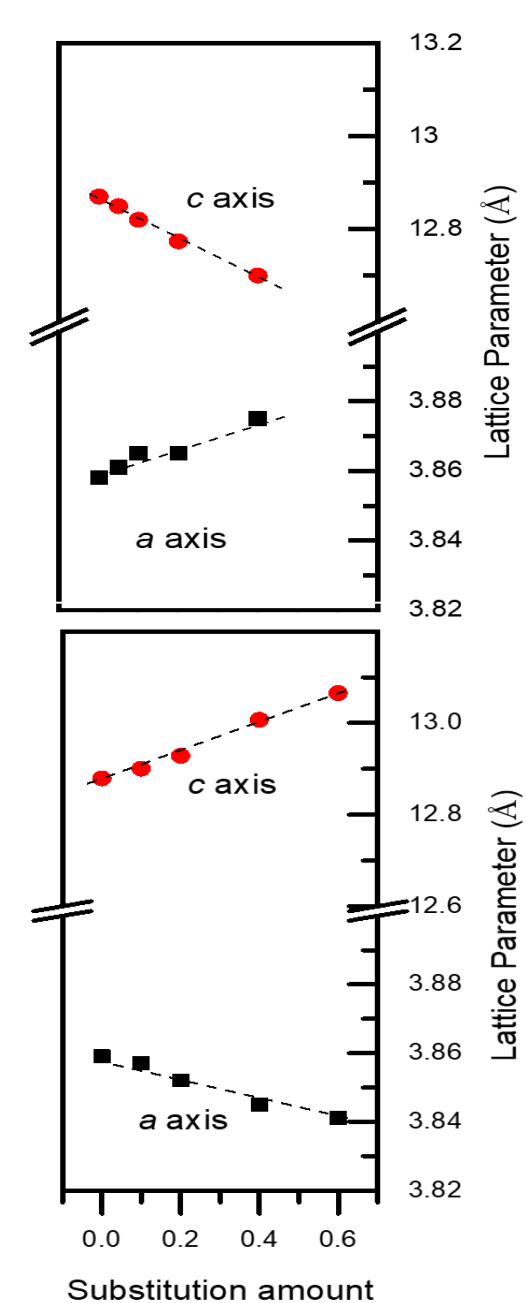
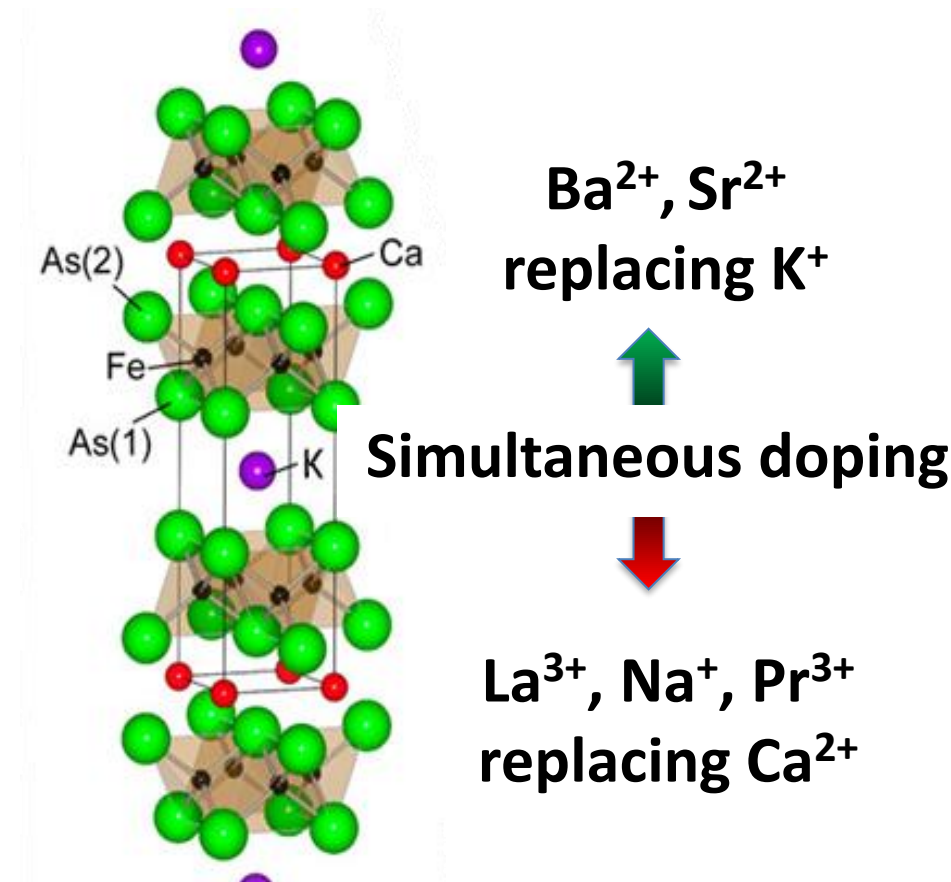
Polycrystalline  $\text{CaKFe}_4\text{As}_4$  samples partially substituted with alkali, alkaline-earth, and rare-earth elements (Na, Ba, Sr, La, and Pr) were synthesized by high-energy ball milling followed by heat treatment at  $800\text{ }^\circ\text{C}$  under an Ar atmosphere. The samples have the general composition  $\text{Ca}_{1-x}\text{K}_{1-y}\text{Fe}_4\text{As}_4$ , where (x) and (y) denote the substitution level. For simplicity, compositions are identified by their nominal dopant content (e.g.,  $\text{Ca}_{0.95}\text{La}_{0.05}\text{KFe}_4\text{As}_4$  is denoted as La5%).

**Aliovalent substitution:**  
different valence (alkaline  $\leftrightarrow$  alkaline earth,  $\rightarrow$  rare earth) – similar ionic radius

**Lattice parameter variation with substitution content.**

**Influence of  $T_c$  on the variation of lattice parameters induced by substitutions.**

**Influence of Critical current density  $J_c(H)$  for  $\text{CaKFe}_4\text{As}_4$  pristine and substituted samples.**



**Influence of Na10%Ba5% and La5% substitution on bare  $\text{CaKFe}_4\text{As}_4$  pristine sample:**

$$J_{c,sf}: 1.3 \cdot 10^4 \text{ A/cm}^2 \rightarrow 2.2 \cdot 10^4 \text{ A/cm}^2 \rightarrow 2.9 \cdot 10^4 \text{ A/cm}^2$$

**Main findings:**

1) The superconducting critical temperature  $T_c$  is closely linked to the crystallographic distortion induced by chemical substitution. The highest  $T_c$  values are found for samples with a (c/a) ratio close to that of pristine  $\text{CaKFe}_4\text{As}_4$ , as illustrated by the Na10%Ba5% sample: Ba and Na substitutions individually suppress  $T_c$  by inducing opposite lattice distortions, while their combined effect restores the (c/a) ratio and partially recovers  $T_c$ .

2) Chemical substitution also enhances the critical current density  $J_c$  compared to the pristine compound, although its origin was still unclear and may involve either grain-boundary chemistry or the introduction of flux-pinning defects.



To clarify this, **chemically substituted single crystals** were grown to remove **grain-boundary effects** and isolate the **contribution of substitution-induced defects** to the  $J_c$  enhancement via flux pinning.

## METHOD

Step I: Crystal growth from the flux method  $\rightarrow$  Step II: Thermal Treatment  $\rightarrow$  Step III: Single crystals  $\rightarrow$  Step VI: Experimental measurements.

**Preparation:**

- 1) FeAs flux prepared in vacuum
- 2) The sequence of precursors selected by melting point to avoid possible evaporation.
- 3) Sealed in steel in Ar glove box

Ar glove box ( $\text{O}_2 < 0.5\text{ ppm}$ ,  $\text{H}_2\text{O} < 5\text{ ppm}$ )

**$\text{N}_2$  flow prevents reactor oxidation during heating**

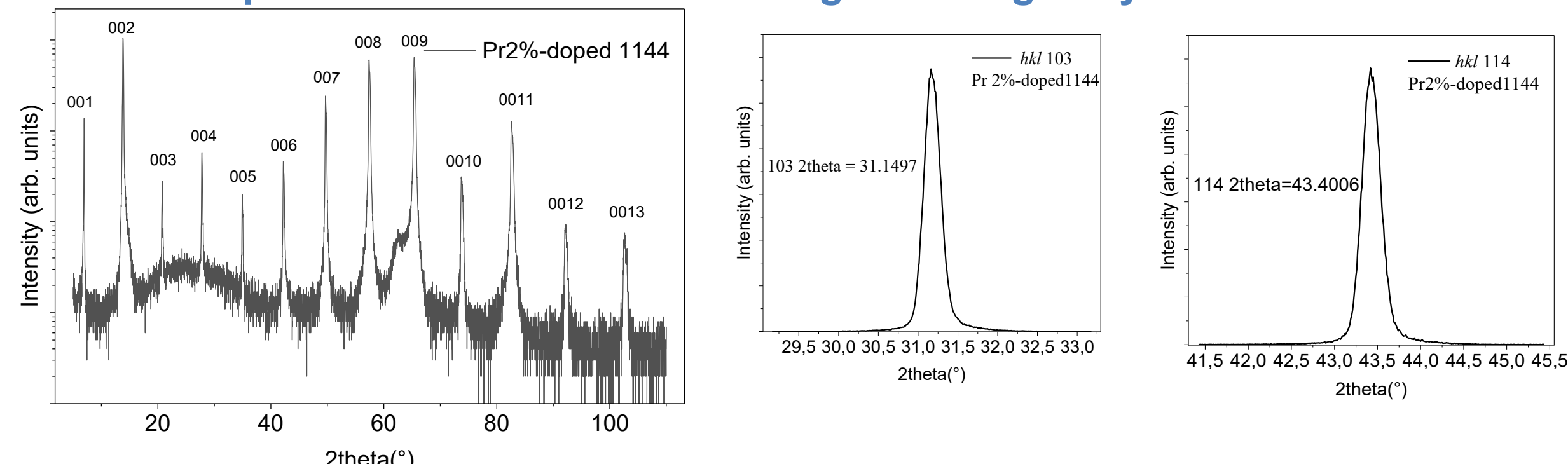
- $T_{\text{max}} = 1200^\circ\text{C}$
- $t = 4/5$  days

**Single crystals obtained:**

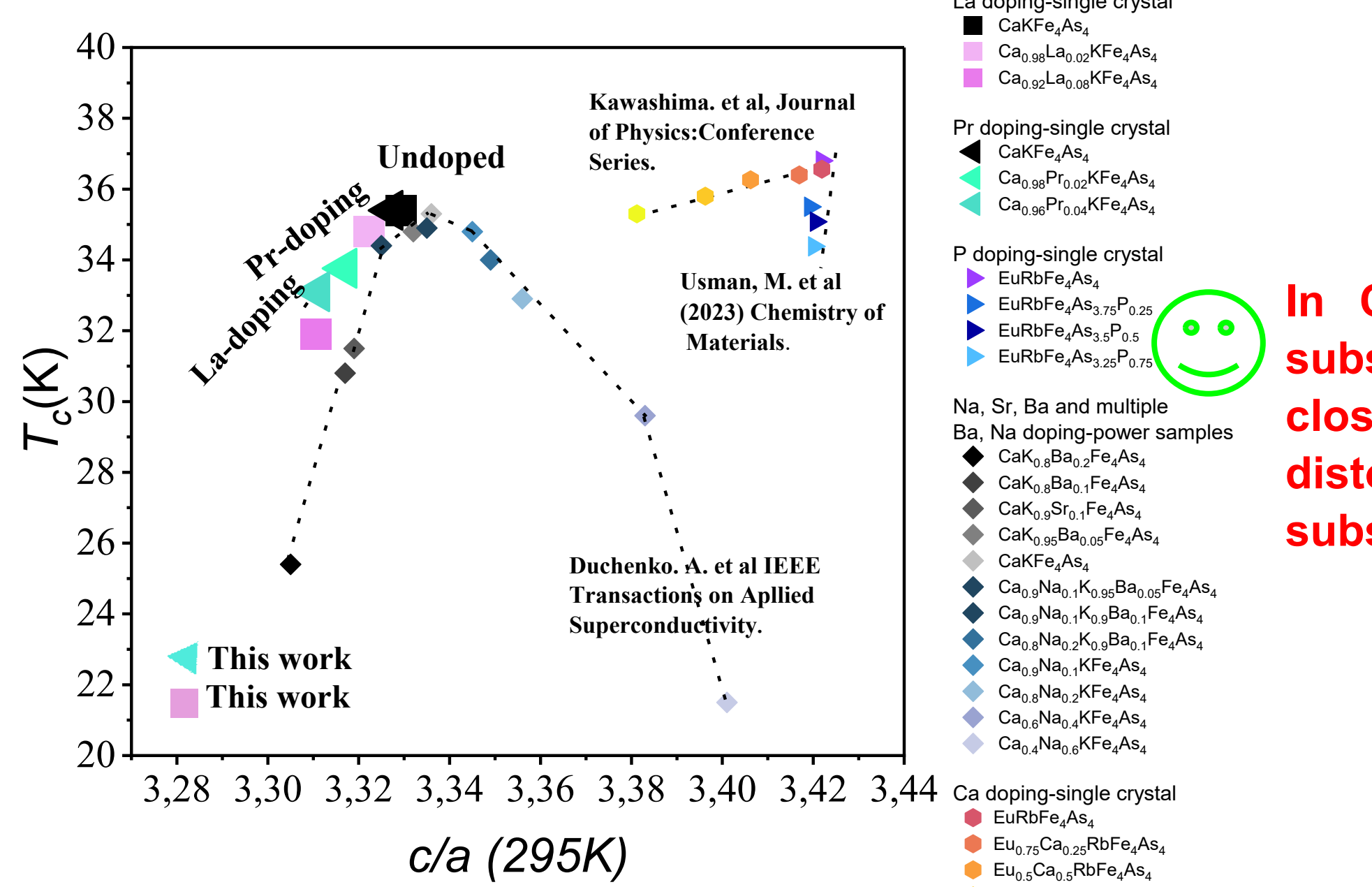
- $\text{CaKFe}_4\text{As}_4$
- Na (1.5%)
- Pr (2–5%)
- La (2–11%)

## RESULTS & DISCUSSION

**20– $\theta$  XRD pattern of the Pr-doped single crystal and enlarged  $\theta$ – $2\theta$  scans of the (103) and (114) reflections. This method was used to determine the lattice parameters a and c for all the grown single crystals.**

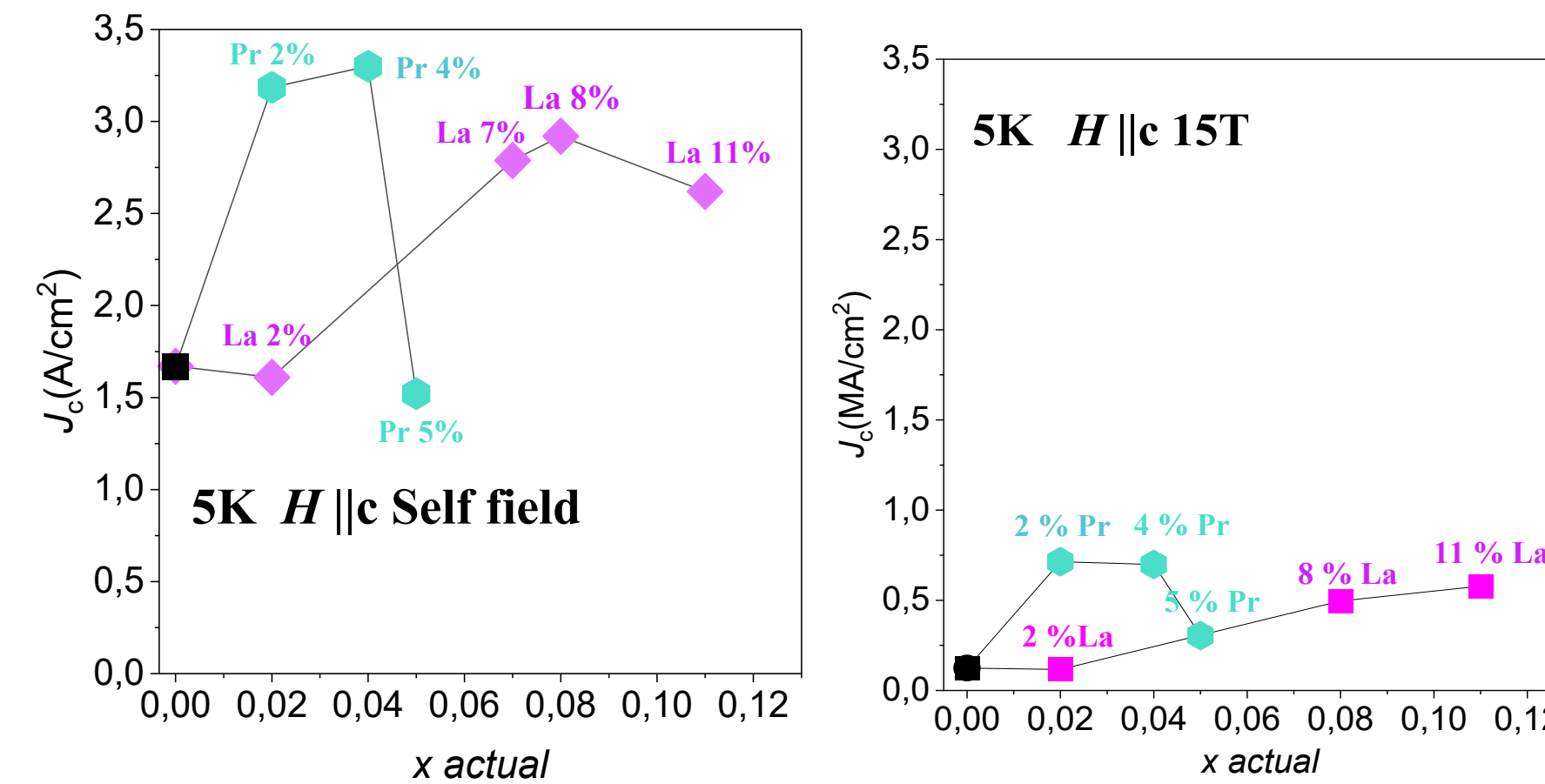


**Relationship between  $T_c$  and lattice distortion c/a in substituted 1144 compounds, including new La- and Pr-doped  $\text{CaKFe}_4\text{As}_4$  single crystals.**



**In  $\text{CaKFe}_4\text{As}_4$  compounds, the substitution at the Ca/K sites is closely linked to the lattice distortion induced by chemical substitution.**

**Critical current density  $J_c$  versus substitution level x for the La- and Pr-substituted  $\text{CaKFe}_4\text{As}_4$  series.**



**Influence of chemical substitution with La and Pr on bare  $\text{CaKFe}_4\text{As}_4$  pristine sample:**

- Chemical substitution with Pr and La enhances  $J_c$
- Strongest at 5K and 15T



## CONCLUSIONS

The increase in  $J_c(H)$  was also observed in single crystals, suggesting that the enhancement induced by chemical substitution mainly originates from newly introduced defects acting as additional pinning centers due to nanostructural effects, rather than from modifications to the chemical nature of grain boundaries.

## REFERENCES

1. Masi A. *et al.*, *Supercond. Sci. Technol.*, Art. no. ac6630, 2022, doi:10.1088/1361-6668/ac6630.
2. Augieri A. *et al.*, *IEEE Trans. Appl. Supercond.*, vol. 34, Art. no. 1–5, 2024, doi:10.1109/TASC.2023.3348433.
3. Duchenko A., *IEEE Trans. Appl. Supercond.*, vol. 34, Art. no. 1–5, 2024, doi:10.1109/TASC.2023.3336613.