Abstract:

The *RE*FeAsO (*RE*1111; *RE* = Rare Earth) family of iron-based superconductors (FBS) exhibits the highest superconducting transition temperatures (T_c) among FBS systems, reaching 57–58 K in F-doped SmFeAsO. However, systematic investigations of their intrinsic properties are often hindered by difficulties in sample growth, phase purity, and reproducibility. Motivated by these challenges, this PhD thesis focuses on tuning the superconducting properties of FBS, particularly Sm1111, using high-pressure growth techniques in comparison with conventional synthesis process at the ambient pressure (CSP-AP).

In the first part of this work, the effects of chemical substitution at different crystallographic sites in (Sm/Gd)FeAsO synthesized by CSP-AP are systematically investigated. The influence of fluorine substitution at the O site, copper at the Fe site, and antimony at the As site is examined using X-ray diffraction, microstructural analysis, Raman spectroscopy, and transport and magnetic measurements. Antimony substitution induces lattice expansion and structural disorder, leading to monotonic suppression of T_c and critical current density (J_c), partly due to the formation of Fe_2Sb impurity phases. Copper acts as a strong impurity scatterer, rapidly suppressing superconductivity and inducing a metal–insulator crossover. Optimized synthesis of $GdFeAsO_{1-x}F_x$ yields high-quality samples with $T_c \approx 43$ K and $J_c \approx 10^3$ A cm^{-2} at 5 K, demonstrating the importance of precursor purity and processing conditions. These results indicate that substitutions within the FeAs layer are more detrimental to superconductivity than those in the *RE*O reservoir layer.

The second part of the thesis focuses on optimizing high-pressure growth of $SmFeAsO_{0.8}F_{0.2}$ using high-gas pressure synthesis, cubic anvil techniques, and spark plasma sintering techniques. With these methods, pressures of up to 6 GPa and temperatures of up to 1800 °C can be applied to identify optimal synthesis conditions. High-pressure processing significantly enhances T_c, J_c, flux pinning, sample density, intergrain connectivity, and compositional homogeneity. *In-situ* synthesis process requires high pressure and temperature (4 GPa, 1400 °C) to complete Sm1111 phase formation and increase T_c by ~3 K, whereas *ex-situ* processing achieves comparable T_c (~55 K) and an order-of-magnitude improvement in J_c at much lower pressure (0.5 GPa). The optimized high-pressure growth conditions extend fluorine doping ($SmFeAsO_{1-x}F_x$; $0.05 \leq x \leq 0.4$), enabling, for the first time, the construction of a comprehensive superconducting phase diagram up to $x = 0.4$. The upper critical field (H_{c2}), estimated using the Werthamer–Helfand–Hohenberg model, reaches ~200 T, indicating strong spin paramagnetic effects and multiband superconductivity. Resistive broadening under applied fields follows Arrhenius behavior, with the activation energy showing a power-law field dependence consistent with collective vortex pinning. In the underdoped region ($0.05 \leq x < 0.2$), the T_c is enhanced by 10-17 K, and the J_c is increased by up to an order of magnitude compared with CSP-AP samples. To demonstrate versatility, high-pressure optimizations are also applied to other FBS such as $FeSe_{0.5}Te_{0.5}$, $CaKFe_4As_4$, and related systems, improving superconducting performance and sample quality.

Overall, this research demonstrates that controlled chemical substitution combined with optimized high-pressure growth provides an effective strategy for enhancing the superconducting properties and phase homogeneity in FBS. These findings provide valuable

insights for the rational design of high-performance superconducting materials for high-field applications, as well as for fundamental studies of superconductivity.