

Abstract

Iron-based superconductors (IBS) provide a diverse platform for investigating the interplay among crystal structure, carrier concentration, magnetism, electronic correlations, vortex dynamics, and superconductivity. Among them, the 1111 ($REFeAsO$; RE = rare earth; $RE1111$) family exhibits high superconducting transition temperatures (T_c up to 58 K), large upper critical fields ($H_{c2} \sim 100$ T), and high critical current densities ($J_c \sim 10^8$ A/cm²). However, systematic studies remain challenging because of the difficulty in obtaining phase-pure and compositionally homogeneous bulk materials over a broad doping range. This thesis focuses primarily on Pr-based iron oxypnictides and develops a systematic approach to understanding and optimizing superconductivity through chemical-pressure tuning, elemental substitution, and high-pressure-assisted synthesis. The work begins with investigations of chemical-pressure and substitution effects in FeSe-based superconductors. Arsenic substitution in FeSe demonstrates the sensitivity of superconductivity to structural modifications and compositional homogeneity, while Pr substitution in $FeSe_{0.5}Te_{0.5}$ modifies the crystal lattice and suppresses competing hexagonal phases at low substitution levels. These studies provide a foundation for extending chemical-pressure tuning to the more complex 1111 family.

A central achievement of this doctoral thesis is the construction of a comprehensive electronic and superconducting phase diagram of fluorine-doped $PrFeAsO_{1-x}F_x$. By combining structural, Raman spectroscopic, density functional theory (DFT), transport, magnetotransport, magnetic, and specific-heat measurements, superconductivity is shown to emerge at $x = 0.15$ and form a broad dome extending to $x = 0.7$, encompassing underdoped, optimal doped, and overdoped regimes. The maximum T_c reaches ~ 52 K at $x = 0.7$. At higher fluorine concentrations, superconductivity disappears as the tetragonal $P4/nmm$ phase is progressively suppressed and a non-superconducting cubic $Fm-3m$ phase emerges for $x = 0.8$ and 1.0 . Large H_{c2} values, short coherence lengths, thermally activated flux flow, and thermodynamic measurements provide complementary insights into the superconducting condensate, vortex dynamics, and electronic structure. Specific-heat analysis confirms the bulk nature of superconductivity and, together with two-gap analysis, supports the multiband character of IBS.

The optimized composition, $PrFeAsO_{0.7}F_{0.3}$, is further used to investigate perturbations within the superconducting FeAs layer. Mn substitution strongly suppresses superconductivity, reducing T_c from ~ 48 K to complete suppression at $x = 0.1$. The simultaneous reduction of H_{c2} and J_c , low-temperature resistivity upturns, and local lattice perturbations identify Mn as a strong magnetic pair-breaking impurity, with the suppression of T_c described by the Abrikosov–Gor’kov model. In contrast, isovalent Sb substitution produces a more gradual suppression of T_c . Moderate Sb substitution modifies H_{c2} and enhances vortex activation energies, indicating changes in vortex dynamics and pinning, whereas higher Sb concentrations introduce substantial lattice disorder and secondary phases that degrade superconductivity and current-carrying capability.

The final part investigates high gas pressure and high-temperature synthesis (HP-HTS) as a growth-engineering strategy. Systematic optimization in $FeSe_{0.5}Te_{0.5}$, $CaKFe_4As_4$, and $Sm1111$ identifies 0.5 GPa and a 1 h dwell time as effective conditions for improving phase formation, T_c , flux pinning, and J_c . Applying these conditions to $PrFeAsO_{1-x}F_x$ with $x = 0.2, 0.3$, and 0.5 improves phase purity, fluorine incorporation, grain connectivity, and intergranular coupling. For $x = 0.3$, the magnetic superconducting transition temperature increases by ~ 6 K compared with conventional solid-state synthesis, while phase segregation at $x = 0.5$ limits the benefits of HP-HTS.

Overall, this thesis establishes a comprehensive framework linking chemical-pressure tuning, crystal structure, electronic and magnetic properties, vortex dynamics, thermodynamics, structural disorder, and growth conditions to superconductivity in IBS. The resulting phase diagram of $PrFeAsO_{1-x}F_x$, systematic substitution studies, and development of pressure-assisted growth strategies provide new

insights into Pr-based 1111 superconductors and identify practical approaches for improving bulk materials toward potential high-field superconducting applications.