2.1 Single-Crystal Growth

2.1.1 SrFe$_2$(As$_{1-x}$P$_x$)$_2$

Single crystals of SrFe$_2$(As$_{1-x}$P$_x$)$_2$ (P-Sr122) except for $x = 0$ and $x = 1$ were grown from a stoichiometric mixture of Sr, FeAs, and FeP powder. FeAs was prepared by reacting Fe powder and As grains at 850°C for 15 h in an evacuated quartz tube. FeP was prepared by reacting Fe powder and P powder at 700°C for 15 h in an evacuated quartz tube.

Sr, FeAs, and FeP were mixed in the atomic ratio 1:2(1 − $x$):2$x$, placed in an alumina crucible, and sealed in a silica tube with Ar gas at 0.2 bar and room temperature. It was heated up to 1300°C, kept for 12 h, and then slowly cooled down to 1050°C at a rate of 2°C/h.

SrFe$_2$As$_2$ ($x = 0$) was grown by the FeAs-flux method. Sr and FeAs were mixed in the atomic ratio 1:4, placed in an alumina crucible, and sealed in a silica tube with Ar gas at 0.2 bar and room temperature. It was heated up to 1200°C, kept for 12 h, and then slowly cooled down to 1050°C at a rate of 2°C/h.

SrFe$_2$P$_2$ ($x = 1$) was grown by the Sn-flux method. Sr, FeP, and Sn were mixed in the atomic ratio 1:2:20, placed in an alumina crucible, and sealed in a silica tube with Ar gas at 0.2 bar and room temperature. It was heated up to 1300°C, kept for 12 h, and then slowly cooled down to 600°C at a rate of 5°C/h. The Sn-flux was removed by a centrifuge.

For comparison, I grew single crystals of BaFe$_2$(As$_{1-x}$P$_x$)$_2$ (P-Ba122) ($x = 0.20$ and 0.25) by the Ba$_2$As$_3$/Ba$_2$P$_3$ flux method described in Ref. [1].

The compositions of the obtained crystals were determined with an electron probe microanalyzer (EPMA) for P-Sr122 and a scanning electron microscope/energy dispersive x-ray spectroscopy (SEM-EDX) for P-Ba122.
2.1.2 \textit{Ba(Fe}_{1−x}\textit{TM}_{x})_{2}\textit{As}_{2} (TM=Cr, Mn, and Co)}

Single crystals of \textit{Ba(Fe}_{1−x}\textit{TM}_{x})_{2}\textit{As}_{2} (TM=Cr, Mn, and Co) were grown by a self-flux method. \textit{MnAs} was prepared by reacting \textit{Mn} powder and \textit{As} grains at 850°C for 15h in an evacuated double sealed quartz tube because it reacts with quartz. Particularly, it is necessary to pay attention to the synthesis of \textit{CrAs}. If the same synthesis conditions as those for \textit{FeAs} are adopted, the quartz tube explodes during the heating. To avoid this problem, a lower amount of the mixture of \textit{Cr} and \textit{As} (\sim 3 g) was loaded into a quartz tube, and the tube was heated to 850°C for 48h and kept for 15h at that temperature.

\textit{Ba}, \textit{FeAs}, and \textit{TMAs} were mixed in the atomic ratio 1:4(1 − \textit{x}):4\textit{x}, placed in an alumina crucible, and sealed in a quartz tube. The tube was heated to 1200°C, kept at that temperature for 10h, and cooled to 1000°C at a rate of 2°C/h. The compositions of the grown crystals were determined by SEM-EDX analysis.

2.1.3 \textit{Post Annealing Treatment}

In \textit{FeSC}, the as-grown single crystals contain various amounts of disorders, lattice dislocations, or defects inside. In order to improve the crystal quality, a post annealing treatment is effective. The post annealing condition depends on the type and size of the crystal. Single crystals of \textit{SrFe}_{2}(\textit{As}_{1−x}\textit{P}_{x})_{2} and \textit{Ba(Fe}_{1−x}\textit{TM}_{x})_{2}\textit{As}_{2} (TM=Cr, Mn, and Co) were sealed in an evacuated silica tube and annealed at 500 and 800°C for several days, respectively.

2.2 \textit{Transport Measurement}

2.2.1 \textit{Resistivity Measurement}

A standard four-probe method was used for the resistivity measurement of twinned and detwinned single crystals.

2.2.2 \textit{Hall Coefficient Measurement}

The Hall resistivity, $\rho_{xy}$, was measured with the electric current along the \textit{ab}-plane and the magnetic field applied along the \textit{c}-axis. The measurement was performed
for magnetic fields up to 7 T at various temperatures by using twinned crystals. The Hall coefficient, $R_H$, was determined by the polynomial fitting of the Hall resistivity with $\rho_{xy} = R_H H + a H^3$, where $H$ is the magnetic field.

### 2.2.3 Resistivity Measurement with Detwinned Crystal

Below the structural transition temperature, $T_s$, the crystal tends to form structural twins, which prevent the measurement of the in-plane anisotropy of iron pnictide. To measure the in-plane anisotropy of the resistivity, a single-domain crystal is required. I detwinned the single crystals by applying a uniaxial pressure along the [110] direction in the tetragonal lattice. The measurements of the in-plane resistivity along both the $a$- and $b$-axes of the orthorhombic lattice were performed on detwinned samples by a standard four-probe method. I repeated the resistivity measurements with increasing pressure and confirmed the saturation of the anisotropy. A schematic picture of the measurement method is shown in Fig. 2.1.

![Fig. 2.1 Schematic picture of a twinned (a) and detwinned (b) crystal. Two sets of domains have the same population for the twinned crystal, whereas one set of domains have a dominant population for the detwinned crystal. (c) and (d) show a schematic picture of a four-probe measurement of the detwinned crystal on the detwinning device, respectively](image-url)
2.3 Magnetization

Magnetization measurements from 1.8 to 300 K were performed using a Quantum Design magnetic property measurement system (MPMS). Zero-field-cooled (ZFC) and field-cooled (FC) data were taken at 10 Oe for superconducting samples.

2.4 X-Ray Diffraction Measurement

The x-ray diffraction experiment of single crystals for determining lattice constants was performed using a four-circle crystal x-ray diffractometer. The x-ray diffraction experiment for the structural analysis of single crystals was carried out using x-ray with 15 keV energy at BL-8A of the Photon Factory, KEK in Japan. In order to determine the atomic positions of SrFe$_2$(As$_{0.65}$P$_{0.35}$)$_2$, I used those of SrFe$_2$As$_2$ as starting parameters and refined them by the least-squares method using Rigaku CRYSTALSTRUCTURE [2].

2.5 Specific Heat Measurement

Specific heat was measured by a relaxation technique down to 1.8 K under magnetic fields up to 14 T using a Quantum Design physical properties measurement system (PPMS).

2.6 Optical Measurement

The optical reflectivity $R(\omega)$ was measured on the $ab$ plane of the mechanically polished samples using Al$_2$O$_3$ powder with a grain size of 0.3 µm and lapping film sheets. The measurement was performed at various temperatures in the frequency range 50–20000 cm$^{-1}$ by a Fourier transform infrared spectrometer at our laboratory, and in the frequency range 20000–320000 cm$^{-1}$ at UVSOR facility, Okazaki, Japan at room temperature. Below 50 cm$^{-1}$, the Hagen–Rubens formula ($R \propto 1 - \alpha \sqrt{\omega}$) was used to extrapolate the optical reflectivity. At a higher energy region (above 320000 cm$^{-1}$), extrapolation with $R \propto \omega^{-4}$ was used.

The optical conductivity was obtained using the Kramers–Kronig relation (KK-relation). The complex reflectivity $\hat{r}(\omega)$ can be obtained as follows.

$$\hat{r}(\omega) = \frac{1 - \sqrt{\varepsilon(\omega)}}{1 + \sqrt{\varepsilon(\omega)}} = \sqrt{R(\omega) \exp(i \theta(\omega))}. \quad (2.1)$$
Here, $\hat{\varepsilon}(\omega)$ is the complex dielectric function, and $\theta(\omega)$ is the phase. $\hat{\varepsilon}(\omega)$ is given as follows.

$$ \hat{\varepsilon}(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega), $$  \hfill (2.2)

$$ \varepsilon_1(\omega) - 1 = \frac{2}{\pi} P \int_0^\infty \frac{\omega'\varepsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega', \hfill (2.3) $$

$$ \varepsilon_2(\omega) = -\frac{2\omega}{\pi} P \int_0^\infty \frac{\varepsilon_1(\omega')}{\omega'^2 - \omega^2} d\omega'. \hfill (2.4) $$

Here, $P$ denotes the principal value.

$R(\omega)$ is experimentally measured, following which the phase $\theta(\omega)$ can be calculated with the KK-relation as follows.

$$ \theta(\omega) = -\frac{2\omega}{\pi} P \int_0^\infty \frac{\ln \sqrt{R(\omega')}}{\omega'^2 - \omega^2} d\omega'. \hfill (2.5) $$

Once the real and imaginary part of the complex reflectivity are calculated, the complex dielectric function can be obtained.

The complex optical conductivity $\hat{\sigma}(\omega) = \sigma_1(\omega) + i\sigma_2(\omega)$ is obtained with dielectric functions as follows.

$$ \sigma_1(\omega) = \frac{\omega \varepsilon_2(\omega)}{4\pi}, \hfill (2.6) $$

$$ \sigma_2(\omega) = \frac{\omega(1 - \varepsilon_1(\omega))}{4\pi}. \hfill (2.7) $$

The Drude-Lorentz model for the dielectric function $\hat{\varepsilon}(\omega)$ was used to describe the optical conductivity.

$$ \hat{\varepsilon}(\omega) = \varepsilon_\infty + \sum_j \frac{\omega_{p,D,j}^2}{\omega^2 + i\omega/\tau_{D,j}} + \sum_k \frac{\Omega_k^2}{\omega_k^2 - \omega^2 - i\omega\gamma_k}. \hfill (2.8) $$

Here, $\varepsilon_\infty$ is the real part of the dielectric function at a high frequency, and $\omega_{p,D,j}^2 = 4\pi n_j e^2/m^*_j$ and $1/\tau_{D,j}$ are the square of the plasma frequency and scattering rate for the Drude carrier in the $j$th Fermi surface, respectively. $n_j$ and $m^*_j$ are the carrier density and carrier mass for the carrier in the $j$th Fermi surface, respectively. $\omega_k$, $\gamma_k$, and $\Omega_k$ are the position, width, and strength of the $k$th vibration or excitation, respectively.

References

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