Single crystals of superconducting SmFeAsO1–xFy grown at high pressure

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Single crystals of superconducting $SmFeAsO_{1-x}F_y$ grown at high pressure

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Abstract. Single crystals of $SmFeAsO_{1-x}F_y$ of a size up to 100x100 μm^2 have been grown from NaCl/KCl flux at pressure of 30 kbar and temperature of 1350-1450 °C using cubic anvil high-pressure technique. Superconducting transition temperature of the obtained single crystals varies between 45 and 53 K. Structure refinement has been performed on single crystal. Differential thermal analysis investigations at 1 bar Ar pressure show decomposition of $SmFeAsO_{1-x}F_y$ at 1302 °C.

1. Introduction

Recent discovery of superconductivity in a family of quaternary oxypnictides with a general formula LnFeAsO (where Ln = La, Ce, Pr, Nd, Sm, Gd) has caused an excitement in the scientific community [1-6]. Crystal structure of PrFeAsO was reported by Quebe et al. [7]. These compounds crystallize with the tetragonal layered ZrCuSiAs structure, in the space group of P4/nmm, which has a structure of alternating LnO and FeAs layers, which are electrically charged and can be represented as $(LnO)^{+\delta}(FeAs)^{-\delta}$ (Fig. 1). Covalent bonding is dominant in the layers, while between layers dominates ionic bonding. The charge carriers in these compounds are electrons confined to the FeAs layers. The LnO layer serves as a "charge reservoir", when doped with electrons. This can be done by partial substitution of O^{2-} by fluorine F^- [2-5], or by generation of oxygen vacancies at high pressure of 60 kbar [6]. The highest critical temperatures above 50 K have been observed for $LnFeAsO_{1-x}F_x$ with Ln = Sm, Gd, Pr and Nd. Both methods of doping lead to decrease of lattice parameters, which indicates, that high pressure can promote such reactions. The presence of two structural blocks namely conducting FeAs layers and "charge reservoir" LnO layers reminds high-T_c cuprates. One can expect, similarly like in cuprates, strong anisotropy of superconducting properties, such as upper critical fields, coherence length and penetration depth. Knowledge of these anisotropic properties is crucial for the understanding of the mechanism of superconductivity in this family of compounds and for their potential applications.

The two techniques have been used for the synthesis of polycrystalline samples: low-pressure quartz ampoule method [1-3] and high-pressure synthesis [4-6]. As a precursor a mixture of LnAs, FeAs, Fe_2O_3, Fe and LnF_3 is usually used. In the low-pressure method, the necessary reaction temperature range of 1150-1250 °C is on the limit of quartz ampoule application due to reaction with precursor, especially with fluorine vapours. In the high-pressure method precursor mixture is placed in BN crucible and synthesized at pressure of 30 to 60 kbar at

temperature 1250-1350 °C during several hours. As results sintered polycrystalline samples with a μm grain size have been obtained. Until now all physical measurements have been performed on polycrystalline samples obtained by one of these ways. As the mechanism of superconductivity in these pnictide oxides is unknown, single crystals are necessary for the investigations of intrinsic anisotropic properties such as upper critical fields, coherence length or penetration depth. Especially for spectroscopic techniques such as Scanning Tunnelling Spectroscopy, Angle-Resolved Photoemission Spectroscopy, Point Contact Spectroscopy, optical investigations etc. studies on single crystals are crucial. In the low- pressure method for the iron arsenide synthesis NaCl/KCl flux has been reported as a mineralizer, which enhances the formation of the quaternary compounds [7]. The authors emphasized, that at the conditions of synthesis (800 °C) only minor amounts of the metallic component were dissolved. We decided to apply this method at high-pressure, which allow us to use also higher temperature. Up to now, the growth of superconducting single crystals of $LnFeAsO_{1-x}F_x$ has not been reported. In this paper we report on the growth and properties of the $SmFeAsO_{1-x}F_y$ single crystals.

2. Experimental

For the synthesis of polycrystalline samples and single crystals of $SmFeAsO_{1-x}F_y$ we used cubic anvil high-pressure technique which has been applied in our laboratory also for the single crystal growth of MgB_2 and other superconductors. Polycrystalline samples of nominal composition $SmFeAsO_{0.8}F_{0.2}$ were prepared using SmAs, FeAs, Fe_2O_3, Fe and SmF_3 powders as starting materials. For the growth of single crystals we used same components and NaCl/KCl flux. The precursor to flux ratio varies between 1:1 and 1:3. The mixing and grinding of precursor powders and pressing pellets have been performed in a glove box due to toxicity of arsenic. Pellets containing precursor and flux were placed in BN crucible inside a pyrophyllite cube with a graphite heater. The six tungsten carbide anvils generated pressure on the whole assembly. In a typical run, a pressure of 3 GPa was applied at room temperature. While keeping pressure constant, the temperature was ramped up within 1 h to the maximum value of 1350-1450 °C, kept for 4-10 h and decreased in 5-24 h to room temperature for the crystal growth. For the synthesis of polycrystalline samples the maximum temperature was kept for 2-4 h followed by quenching. Then pressure was released, sample removed and in the case of single crystal growth NaCl/KCl flux dissolved in water. One has to mention that such high-pressure experiments have to be performed very carefully, because explosion during heating due to increased pressure in the sample container can lead to a contamination of the whole apparatus with arsenide compounds. Differential thermal analysis (DTA) was carried out in a Perkin Elmer DTA 7 analyzer using Al_2O_3 crucibles in flowing Ar with a heating rate

of 5°C/min up to 1600 °C. The magnetization was measured with a Quantum Design SQUID magnetometer. Structural investigations have been done using an X-ray diffractometer equipped with charge-coupled device (CCD) detector (Xcalibur PX, Oxford Diffraction). Data reduction and analytical absorption correction were performed using the program CrysAlis [8]. The crystal structure was determined by direct method and refined on F^2, employing the programs SHELXS-97 and SHELXL-97 [9, 10].

3. Results

In order to determine temperature limits for the crystal growth in ambient pressure DTA investigations in 1 bar Ar pressure were performed. For this experiment polycrystalline sample of $SmFeAsO_{1-x}F_y$ obtained at high pressure was used. The results of the run are shown in Fig. 2. One can notice two endothermic peaks corresponding to two reactions. First one, with an onset at 993 °C and a maximum at 1020 °C, corresponds to melting of FeAs, which was an impurity in our $SmFeAsO_{1-x}F_y$ sample. Second one, with an onset at 1302 °C, corresponds to incongruent melting of $SmFeAsO_{1-x}F_y$. This practically excludes increasing temperature for the crystal growth at ambient pressure much above 1250 °C used usually for the synthesis of polycrystalline samples. Samples obtained at this temperature have very fine μm size grains. With the aim of growing single crystals suitable for physical measurements, we carried out a systematic investigation of the parameters controlling the growth of crystals, including temperature, pressure, composition, reaction time and heating/cooling rate. As result of the crystal growth experiments $SmFeAsO_{1-x}F_y$ platelike crystals have been obtained. Crystals of a size about 100x100x20 μm^3 grown in this way are presented in Fig. 3.

3.1. Crystal structure

All atomic positions were found by direct method. The structure was refined without any restrains. Oxygen and fluorine atoms which occupy the same site are impossible to distinguish with XRD, so they were treated during refinement as one atom. The results of the structure refinement are presented in Tables 1 and 2.

Table 1. Crystal data and structure refinement for the $SmFeAsO_{0.86-x}F_x$

Empirical formula	$SmFeAsO_{0.86-x}F_x$
Temperature, K	295(2)
Wavelength, Å	0.71073/MoKα
Crystal system, space group, Z	Tetragonal, *P*4/nmm, 2
Unit cell dimensions, Å, deg	*a*= 3.93390(10), *c*= 8.4684(6),
Volume, $Å^3$	131.053(10)
Calculated density, g/cm^3	7.49
Absorption correction type	analytical
Absorption coefficient, mm^{-1}	39.914
F(000)	257
Crystal size, μm^3	70 x 30 x 10
Theta range for data collection	4.81 to 37.19 deg.
Index ranges	-5=h<=6, -6<=k<=6, -14<=l<=13
Reflections collected/unique	867/235 $R_{int.}$= 0.0399
Completeness to 2theta	97.5 %
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	235/0/12
Goodness-of-fit on F^2	1.017
Final R indices [I>2sigma(I)]	R_1 = 0.0323, wR_2 = 0.0708
R indices (all data)	R_1 = 0.0461, wR_2 = 0.0746
$\Delta\rho_{max}$ and $\Delta\rho_{min}$,(e/A^3)	3.594 and -2.454

Table 2. Atomic coordinates and equivalent isotropic and anisotropic displacement parameters [$Å^2$ x 10^3] for the $SmFeAsO_{0.86-x}F_x$

Atom	Site	x	y	z	U_{iso}	U_{11}=U_{22}	U_{33}
Sm	2*c*	-1/4	-1/4	0.1411(1)	11(1)	10(1)	12(1)
Fe	2*b*	1/4	3/4	1/2	10(1)	10(1)	10(1)
As	2*c*	1/4	1/4	0.3391(2)	10(1)	9(1)	12(1)
O(F)	2*a*	1/4	3/4	0	11(3)	10(3)	15(5)

U_{iso} is defined as one third of the trace of the orthogonalized U_{ij} tensor. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [(h^2a^2U_{11} + ... + 2hka^*b^*U_{12}]$. For symmetry reasons U_{23}=U_{13}=U_{12}=0.

The results are in good agreement with the published data for the PrFeAsO [7]. According to the reflection conditions for the space group P4/nmm (*hk*0 = 2n) the systematic absences occur only for the *hk*0 reciprocal section (Fig. 4). Structural analysis revealed overall occupancy in the O(F) site considerably lower than 100 % equal to 0.86. Therefore it is possible, that except F doping we have also additional electron doping due to O vacancies. However, the accuracy of the oxygen or fluorine occupancy factor is very low because of presence of such heavy atoms like As, Fe and Sm in the unit cell. The residuals w*R* and wR_2 as well as goodness of fit *S* show small difference for the oxygen occupancy of 86 % and 100 % (Tab. 3). The minimal residuals correspond to the $O(F)_{occ.}$ of 86 ± 3 at. %. Neutron diffraction data could be helpful for clarifying this point.

Table 3. Residuals and Goodness of fit for the different number of O(F) occupations in the $SmFeAsO_{1-x}F_y$

$O(F)_{occ.}$, *at. %*	w*R*	wR_2	*S*
86	0.0461	0.0746	1.017
100	0.0474	0.0771	1.050
0	0.0849	0.1554	2.120

3.2. Superconducting properties

Magnetic measurements of such crystals show that T_c varies between 45 and 53 K dependently on growth conditions. Figure 4 shows the temperature dependence of magnetic susceptibility measured on the collection of single crystals from one batch. The measurements were carried out in a magnetic field of 5 Oe on heating after zero-field cooling and then on cooling in a field. A superconducting volume fraction is large enough to constitute bulk superconductivity. Maximum T_c reported for this compound is 55 K. Lower T_c indicates non-optimal doping.

4. Conclusion

Single crystals of $SmFeAsO_{1-x}F_y$ superconductor have been grown for the first time using high pressure cubic anvil technique. The crystals have a plate like shape with size up to 100 μm and are superconducting below 51-53 K. The crystal structure of $SmFeAsO_{1-x}F_y$ refined from single crystal x-ray diffraction data shows incomplete occupancy of O(F) position.

Acknowledgments

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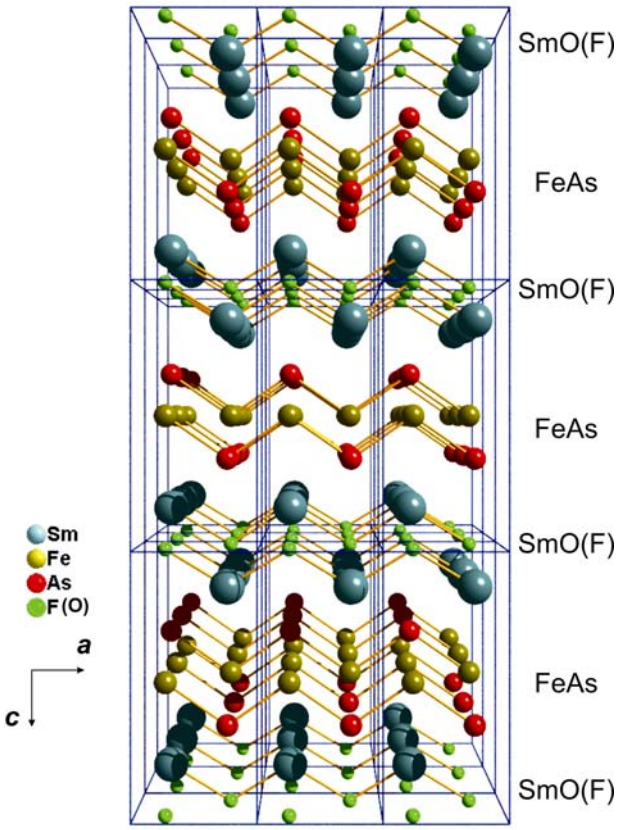

Figure 1. Schematic representation of the 3x3x3 unit cells of $SmAsFeO_{1-x}F_y$ along the *a* direction.

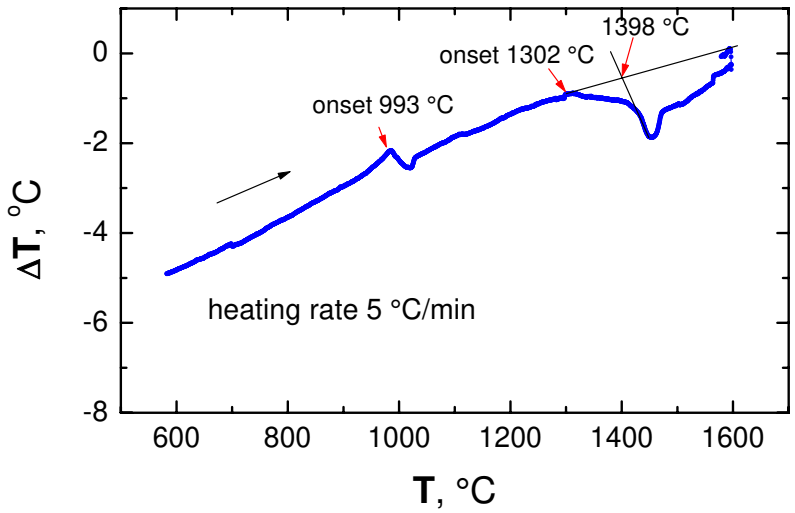

Figure 2. Differential thermal analysis performed in 1 bar Ar on $SmAsFeO_{1-x}F_y$ polycrystalline sample showing decomposition onset (incongruent melting) at 1302 °C.

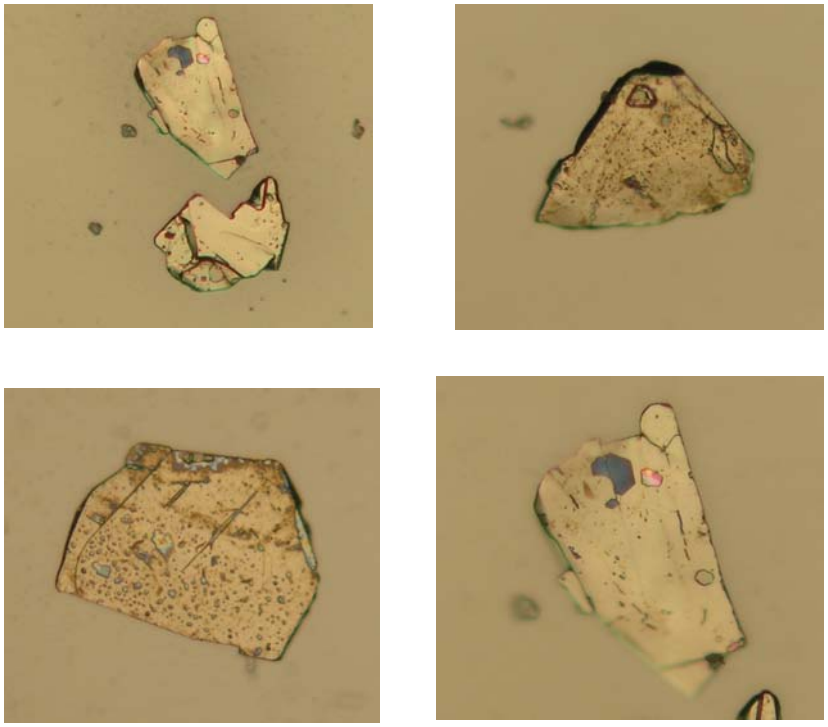

Figure 3. $SmFeAsO_{1-x}F_y$ single crystals grown from NaCl/KCl flux at high pressure. The length of crystals is about 100 μm.

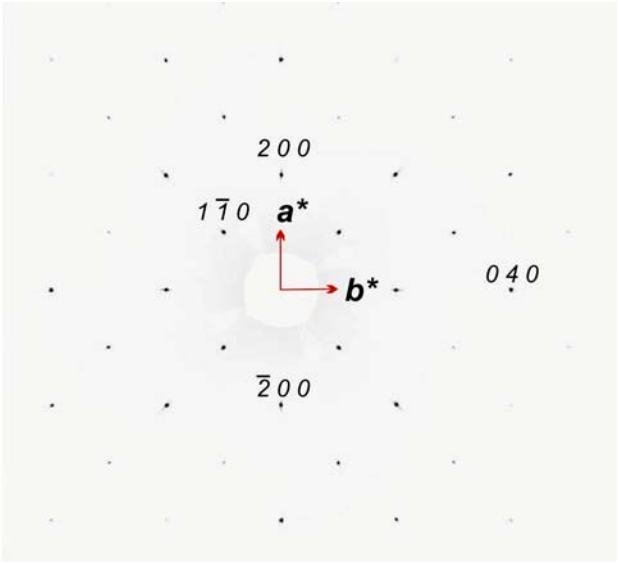

Figure 4. The reconstucted *hk0* reciprocal space section of the $SmFeAsO_{1-x}F_y$ single crystal.

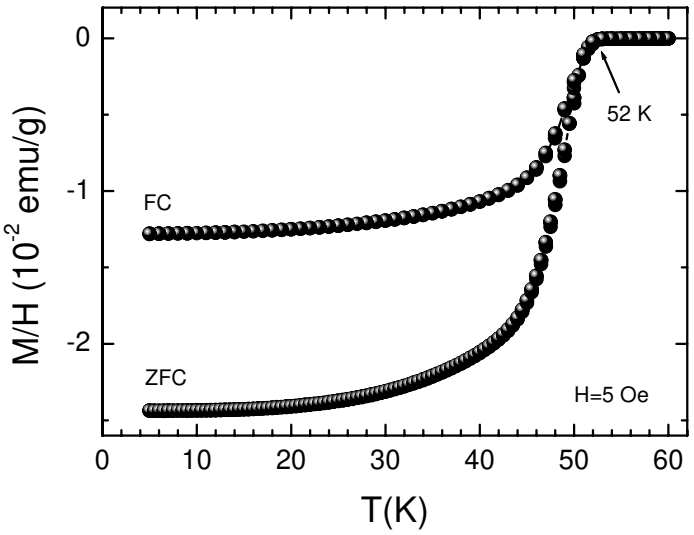

Figure 5. Temperature dependence of magnetic susceptibility measured on a collection of randomly oriented $SmFeAsO_{1-x}F_y$ crystals in an applied field of 5 Oe. ZFC and FC mean zero-field cooling and field cooling curves, respectively.