High-pressure structural phase transitions in chromium-doped BaFe$_2$As$_2$

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Abstract. We report on the results from high pressure x-ray powder diffraction and electrical resistance measurements for hole doped BaFe$_{2-x}$Cr$_x$As$_2$ ($x=0, 0.05, 0.15, 0.4, 0.61$) up to 81 GPa and down to 10 K using a synchrotron source and diamond anvil cell (DAC). At ambient temperature, an isostructural phase transition from a tetragonal (T) phase ($I4/mmm$) to a collapsed tetragonal (CT) phase is observed at 17 GPa. This transition is found to be dependent on ambient pressure unit cell volume and is slightly shifted to higher pressure upon increase in the Cr-doping. Unlike BaFe$_2$As$_2$ which superconduct under high pressure, we have not detected any evidence of pressure induced superconductivity in chromium doped samples in the pressure and temperature range of this study. The measured equation of state parameters are presented for both the tetragonal and collapsed tetragonal phases for $x=0.05, 0.15, 0.40$ and 0.61.

1. Introduction
The discovery of pressure enhanced superconductivity in chemically doped iron arsenide compounds in 2008 [1] has attracted extensive research activities on these materials in the field of high pressure physics [2]. One of the most intensively investigated iron-based compound is BaFe$_2$As$_2$ with the tetragonal ThCr$_2$Si$_2$ (122) type crystal structure [3, 4]. At ambient pressure, pure BaFe$_2$As$_2$ is known to undergo a crystallographic phase transition from a tetragonal phase ($I4/mmm$) to an orthorhombic phase ($Fmmm$) and a concurrent antiferromagnetic ordering (spin-density wave, SDW) at ~140 K [3]. The transition is suppressed by either chemical doping or application of high pressure resulting in the appearance of superconductivity [3, 4]. Ambient pressure studies show that hole-doping using chromium leads to suppression of the magnetic and structural transitions, but does not lead to superconductivity [5]. Studies under pressure have shown that BaFe$_2$As$_2$ interestingly undergoes an isostructural phase transition from tetragonal (T) phase to an isostructural collapsed tetragonal (CT) phase which is accompanied by anomalous compressibility effect and a sharp drop in axial ratio $c/a$ [6-8]. In the present work, we present high pressure electrical resistivity and x-ray diffraction measurements on hole doped BaFe$_{2-x}$Cr$_x$As$_2$ up to 81 GPa and down to 10 K using a synchrotron source and diamond anvil cell. We investigate the influence of chemical doping and high pressure on the tetragonal crystal structure and the possibility of the pressure induced superconductivity.
2. Experimental Methods

Single crystals of BaFe$_{2-x}$Cr$_x$As$_2$ were grown out of a mixture of FeAs and CrAs flux and characterized by x-ray diffraction and electron probe micro-analysis as described in the original publication [5]. The crystals were ground and loaded into an 80-micron hole of a spring-steel gasket that was first pre-indented to a ~ 50-micron thickness and mounted between a matched pair of beveled diamond anvil cell ready for high-pressure experiments.

The synchrotron x-ray powder diffraction experiments were performed at the high pressure beamline 16-ID-B of the Advanced Photon Source (APS) in Argonne National Laboratory. An angle dispersive technique with a MAR345 image-plate area detector was employed using a focused monochromatic beam with x-ray wavelength, $\lambda = 0.4246$ Å. The image plate x-ray diffraction patterns were recorded with a focused x-ray beam of 5μm by 5μm on an 80 μm diameter sample mixed with powdered copper pressure marker. Experimental geometric constraints and the sample to image plate detector distance were calibrated using CeO$_2$ diffraction pattern. The lattice parameters of the copper pressure marker obtained from the Rietveld refinement of the x-ray diffraction patterns of copper-powder mixed with the sample in the DAC were employed for the calibration of pressure [9]. At ambient temperature, the Birch-Murnaghan equation [10] as shown by equation (1) was fitted to the available equation of state data on copper pressure standard [9] to determine sample pressure.

$$ P = \frac{3}{4} B_0 \left[ \left( \frac{V_0}{V} \right)^{7/3} - \left( \frac{V_0}{V} \right)^{5/3} \right] \left[ 1 + \frac{3}{4} (B'_0 - 4) \left( \frac{V_0}{V} \right)^{2/3} - 1 \right] $$ (1)

Where $B_0$ is the bulk modulus, $B'_0$ is the first derivative of bulk modulus at ambient pressure, and $V_0$ is the ambient pressure volume. The fitted values for the copper pressure standard are $B_0 = 121.6$ GPa, $B'_0 = 5.583$, and $V_0 = 11.802$ Å$^3$/atom [9]. We employed the software package FIT2D [11] to integrate the collected MAR3450 image plate diffraction patterns. The integrated patterns were analyzed by EXPGUI/GSAS software [12] using full-pattern Rietveld refinements and LeBail fit techniques to extract structural parameters.

3. Results and discussion

At room temperature and nearly ambient pressure (P~ 0.1±0.2 GPa), BaFe$_{2-x}$Cr$_x$As$_2$ samples are all identified as ThCr$_2$Si$_2$ (I4/mmm) with the following measured lattice parameters: a = 3.962Å(18), c = 13.0760(20)Å and $V_0 = 205.3$ Å$^3$ for BaFe$_{1.95}$Cr$_{0.05}$As$_2$; $a = 3.9615(21)$ Å, $c = 13.1731(13)$Å and $V_0 = 206.7$Å$^3$ for BaFe$_{1.85}$Cr$_{0.15}$As$_2$; $a = 3.9682(15)$ Å, $c = 13.1671(8)$Å and $V_0 = 207.3$Å$^3$ for BaFe$_{1.6}$Cr$_{0.4}$As$_2$; $a = 3.9705(21)$ Å, $c = 13.2397(22)$Å and $V_0 = 208.7$Å$^3$ for BaFe$_{1.38}$Cr$_{0.6}$As$_2$. The incorporation of Cr in to Fe site is observed to increase the unit cell volume without any evidence of a structural phase transition and this is in good agreement with previous ambient pressure studies [5].

Figure 1(a) shows the measured axial ratios (c/a) as a function of pressure at ambient temperature for hole doped BaFe$_{2-x}$Cr$_x$As$_2$. For x = 0.05, c/a ratio show a rapid decrease (~21% decrease) with increasing pressure up to ~16.9 GPa and a gradual decrease above this pressure. The c/a ratio variation as a function of pressure can be divided into two linear regions and the fits for the two linear regions are shown as solid lines in the figure. The intersection of the two linear regions defines the phase transition pressure from the ambient pressure T-phase to the CT-phase. The T-CT phase transition is defined by the present experiments to occur at ~17 GPa. We made similar observations at ambient temperature for the case of x = 0.15, x = 0.4 and x = 0.61 with the T-CT phase transitions shifting slightly to ~19.8 GPa, ~14.8 GPa and ~20.3 GPa respectively.
Using equation (2) and the measured volume \( V_0 \) given above, we predicted the T-CT transitions for the series of BaFe\(_2-x\)Cr\(_x\)As\(_2\) to occur at \( P_{CT}=16.4 \) GPa, 17.0 GPa, 17.2 GPa and 17.7 GPa for \( x=0.05, 0.15, 0.4 \) and 0.61 respectively and these are in consistent with the measured values shown in table 1. The measured equations of state show considerable stiffening at the tetragonal to collapsed tetragonal phase transition and the T-CT transition shift slightly to higher pressure value as evidenced by the measured volume-pressure curves as depicted in figure 1(b). The solid lines in (b) indicate Birch Murnaghan equation of state fit to data in T and CT phases. Figure 1 (c) shows the normalized temperature dependence of electrical resistance for pressures up to 22.2 GPa and temperatures below 100 K.

Collecting all the measured data, we predicted the T-CT transition pressure for BaFe\(_2-x\)Cr\(_x\)As\(_2\) compounds can be predicted by equation 2.

\[
P_{CT} = 0.388V_0(\pm0.034)GP\AA^3 - 63.259(\pm6.2)GPa
\]  

Using equation (2) and the measured volume \( V_0 \) given above, we predicted the T-CT transitions for the series of BaFe\(_2-x\)Cr\(_x\)As\(_2\) to occur at \( P_{CT}=16.4 \) GPa, 17.0 GPa, 17.2 GPa and 17.7 GPa for \( x=0.05, 0.15, 0.4 \) and 0.61 respectively and these are in consistent with the measured values shown in table 1. The measured equations of state show considerable stiffening at the tetragonal to collapsed tetragonal phase transition and the T-CT transition shift slightly to higher pressure value as evidenced by the change in slope of the volume-pressure curves as depicted in figure 1(b). The fitted value of bulk modulus \( (B_0) \), pressure derivative of bulk modulus \( (B'_0) \) and unit cell volume \( (V_0) \) at ambient conditions for both T and CT phases are summarized in table 1.

The high-pressure temperature dependence electrical resistance measurements were performed down to 10 K using four-probe method in an eight-probe designer diamond anvil cell as described in our earlier publication [14]. Our resistance data do not show any evidence of superconductivity up to a pressure of 22.2 GPa and down to 10 K as shown in figure 1(c) for BaFe\(_{1.95}\)Cr\(_{0.05}\)As\(_2\). Instead, we observe an upturn in resistance below 80 K and at 0.1 GPa. The resistance decreases with increase in pressure up to 6 GPa. Further increase in pressure above 6 GPa leads to increase in the magnitude resistivity up to 22 GPa. This is in contrast to the results on pure BaFe\(_2\)As\(_2\) in which superconducting transition temperature \( T_C \) with a peak of 34 K at 0.1 GPa was shown to be induced by pressure [6].
show distinct bulk moduli and ambient unit cell volume (\(V_0\)) of the parent compounds. The equation of state for T and CT phases, \(x\) as a function of pressure, is given by (2) below:

\[
\frac{dV}{dp} = \frac{1}{B_0} (B_0 - B) \quad \text{for} \quad T \text{ phase, } x = 0.05
\]

\[
\frac{dV}{dp} = \frac{1}{B_0} (B_0 - B) \quad \text{for} \quad CT \text{ phase, } x = 0.05
\]

The collapsed tetragonal phase, \(x = 0.05\), is correlated to ambient pressure volume of \(\text{BaFe}_{0.57}\text{Cr}_{0.43}\text{As}_2\) at ambient temperature.

In conclusion, our high pressure studies have shown absence of superconductivity and presence of a collapsed tetragonal phase that is correlated to ambient pressure volume of \(\text{BaFe}_{0.57}\text{Cr}_{0.43}\text{As}_2\). The T-CT phase transitions reported here are similar to those observed previously in undoped parents (e.g. \(\text{BaFe}_{0.57}\text{As}_2\)) of Fe-based superconductors. The T-CT transition is dependent on the ambient pressure unit cell volume which increases with concentration of Cr incorporated in Fe site and can be predicted using the equation (2) developed for the parent compounds. The equation of state for T and CT phases show distinct bulk moduli and ambient unit cell volume (\(V_0\)) for all the studied \(\text{BaFe}_{0.57}\text{Cr}_{0.43}\text{As}_2\) samples.

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