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Single crystal growth of the new pressure-induced-superconductor CrAs via chemical vapor transport

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ABSTRACT

Mono-arsenide CrAs, endures a helical anti-ferromagnetic order transition at ~265 K under ambient pressure. Recently, pressure-induced-superconductivity was discovered vicinity to the helical anti-ferromagnetic order in CrAs [Wei Wu et al., Nature Communications 5, 5508 (2014).]. However, the size of crystal grown via tin flux method is as small as 1 mm in longest dimension. In this work, we report the single crystal growth of CrAs with size of 1 × 5 × 1 mm^3 via chemical vapor transport method and its physical properties.

1. Introduction

Since the discovery of superconductivity in rare-earth iron pnictides [1,2], intensive research efforts have been exerted to explore new superconductor in transition metal oxide pnictides, pnictides and chalcogenides [3–7], which leads to booming new superconductors in the past several years. Superconductivity is often found to be in the vicinity of the anti-ferromagnetic (AFM) in newly discovered iron based superconductors. Therefore, it is now widely accepted that the origin of superconductivity is related to the magnetism in iron based superconductors as well as the high temperature cuprates superconductors.

CrAs, a mono-arsnide, adopts a structure of the MnP type, which is tetragonal (space group *Pnma*, 62) with lattice parameters $a = 5.651$ Å, $b = 3.465$ Å, $c = 6.209$ Å. The crystal structure viewed along *b*-axis and *c*-axis is shown in Fig. 1a and b, respectively. Obviously, the crystal structure of CrAs can be regarded as stacking the unit cells along *b*-axis. The Cr atoms are six-fold coordinated by the As atoms, and lie in a zig-zag line along *a*-axis and *c*-axis. For decades ago, neutron diffraction studies demonstrate that CrAs endures a special double helical AFM order transition with a spiral propagation vector of $0.353 \cdot 2\pi c$ [8]. Its Néel temperature (T_N) was reported as 260–270 K [8], 265 K [9], and 240 K [10]. The transition is first order, showing a hysteresis between 260 and 270 K [8]. Below the transition, the *b*-axis lattice parameter *b* increases by about 4%, while the *a*-axis lattice parameter (*a*) and *c*-axis lattice parameter (*c*) decreases by about 0.3% and 0.5%, respectively [11]. Just recently, superconductivity was observed in CrAs under pressure (*P*) when its helical AFM transition was suppressed, by two different groups Wei Wu et al. [12] and Hisashi Kotegawa et al. [13]. The maximum superconducting transition temperature (T_C) is about 2.2 K at critical pressure (P_c) for both groups. The *P* dependent phase diagram is reminiscent of doped iron based superconductors. Moreover, nuclear quadrupole resonance results indicate that it is an unconventional superconductor [14].

The single crystals were grown via tin flux method by both two groups [13,15]. However, the single crystals were as small as about 0.15 × 1 × 0.15 mm^3, which hinders some further physics measurements. Another mono-arsnide, FeAs has been grown successfully via chemical vapor transport (CVT) method [16]. Therefore, it is worthy to try to grow CrAs single crystal via CVT method. In this work, we report the single crystal growth of CrAs with typical size of 1 × 5 × 1 mm^3 via chemical vapor transport method and its physical properties.

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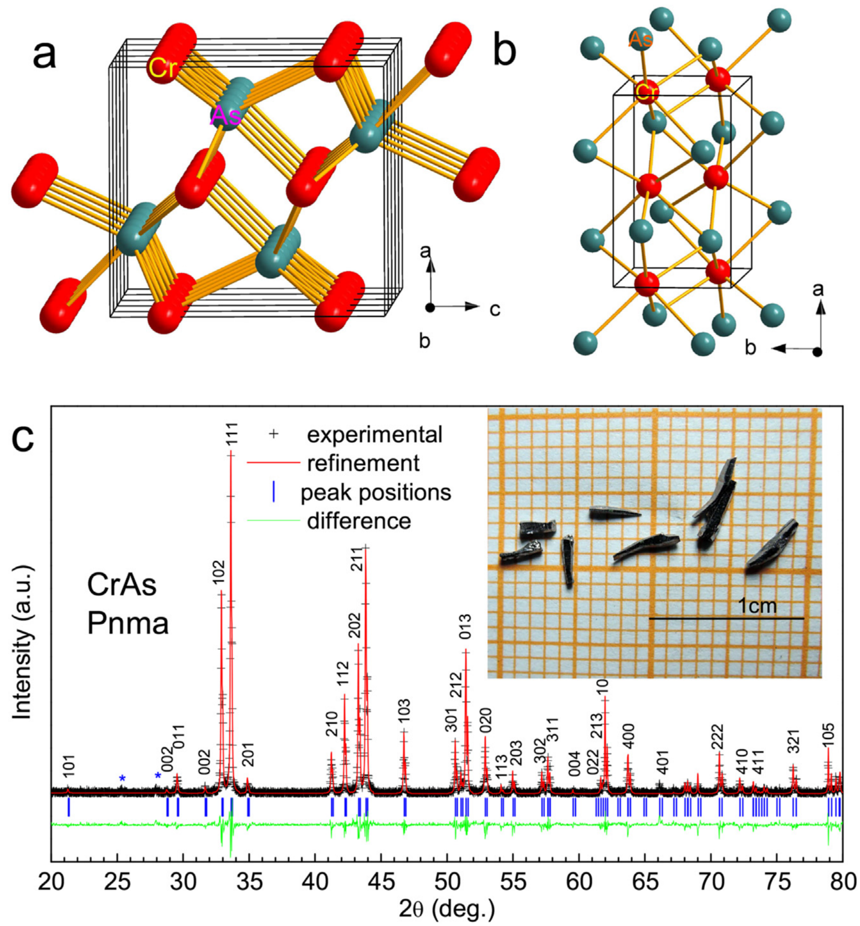

Fig. 1. **a**. The crystal structure viewed from *b*-axis for CrAs. **b**. The crystal structure viewed from *c*-axis for CrAs. **c**. The experimental and refined powder x-ray patterns of CrAs. The calculated peak positions are marked as blue bars. The green line below represents the difference between the experimental and refined data. The inset of *c* shows the photograph of as-grown CrAs single crystal. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2. Material and methods

2.1. Synthesis

The single crystal of CrAs was successfully grown via chemical vapor transport method with iodine as the transport agent. Stoichiometric Cr pieces (99.9%, Alfa), As pieces (99.99%, Aladin), and 50 mg iodine (99.99%, Aladin) were mixed and sealed in an evacuated quartz tube with diameter of 17 mm, and length of ~20 cm. Then the tube was put in a two zone horizonal furnace. First, the temperature of both zone was slowly heated to 800 °C, and kept for four days. Second, the source zone was slowly increased to 900 °C for one week before furnace cooling. Single crystals of CrAs in shape of a helical needle can be found with the size of ~1 × 5 × 1 mm^3, which is shown in Fig. 1b. This size is significantly larger than that of the samples grown via Sn flux method [13,15]. The as-grown crystal is covered by some black powder, which can be erased and cleaned. The cleaned single crystal is stable in air, showing shiny silver-like faces. Arsenic single crystals with hexagonal plate can also been found as a by-product. The as-grown CrAs crystals can be easily cleaved along *b*-axis.

2.2. X-ray diffraction and elemental analysis

Several single crystals were crushed and ground for powder X-ray measurement on the Rigaku-TTR3 x-ray diffractometer using high intensity graphite monochromatized CuK_α radiation. Elemental analysis was performed by using energy-dispersive X-ray spectroscopy (EDS) on an FEI Helios Nanolab 600i. The EDS results gives a Cr:As ratio of 49.82:50.18, which indicates the good stoichiometry of the as-grown sample.

2.3. Transport properties and magnetism

Electrical transport measurement was carried out on a Quantum Design Physical Property Measurement System (PPMS), with the current applied along *b*-axis. Data were collected over a temperature range of 2–300 K. Temperature dependent resistivity measurement were performed using a four-probe configuration. Gold wires were attached on a polished sample with the electrical contacts made of silver paint. The magnetization was measured by a magnetic property measurement system (Quantum Design MPMS 7T-XL) with a superconductive quantum interference device (SQUID).

3. Results and discussions

3.1. X-ray diffraction pattern

Fig. 1 shows the powder x-ray pattern of the CrAs. The peak positions are labeled and consistent with the calculated results from other literature. Some minor peaks can be observed, which