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Depotassiation of $K_{0.62}RhO_2$ and electronic property of the end-product $K_{0.32}RhO_2$ single crystal

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ABSTRACT

K_xRhO_2, as an isomorphism material to Na_xCoO_2, is theoretically predicted to have rich physical properties. In this letter, we studied the chemical depotassiation process of $K_{0.62}RhO_2$ crystals to obtain K_xRhO_2 with x varied from 0.32 to 0.62. And an end-product $K_{0.32}RhO_2$ with *single phase* determined through XRD refinement belongs to space group $P6_3/mmc$ (No. 194). Electrical transport, magnetoresistant transport and Hall measurements substantiate that $K_{0.32}RhO_2$ is a multi-band normal metal, which can be well described by Landau Fermi liquid theory. Our finding sheds more light on the preparation and transport properties of layered oxides.

1. Introduction

In 1997, Terasaki et al. proposed $NaCo_2O_4$ as a thermoelectric material, which exhibits a metallic conductivity and unusually large thermo-power (Seebeck coefficient $\sim$100 μV/K at room temperature) [1]. It was explained as the large spin entropy carried by strongly correlated holes (Co^{4+} sites) hopping on the triangular lattice [2]. Afterwards, Takada *et al.* reported that Na_xCoO_2 intercalated with water becomes a superconductor with T_c=4 K when x is between 1/4 and 1/3 [3]. Then the insulator behavior due to spin or charge ordering was found in Na_xCoO_2 ($x\sim1/2$) [4]. In addition, there is another interesting phenomenon named as coherent-incoherent transition observed in Na_xCoO_2. This phenomenon is: the electrical transport of Na_xCoO_2 mainly lies along each "isolated" quasi-two-dimensional CoO_2 layer at high temperatures, but these "isolated" CoO_2 planes become connected at low temperatures to give a three-dimensional (3D) electrical transport [5,6]. Theoretically, some above-mentioned experimental results were discussed based on electronic band structure predicted by the first-principles calculation [7].

K_xRhO_2 is an isomorphism material to Na_xCoO_2. As shown in Fig. 1(a), K_xRhO_2 is formed by the alternative stacking of RhO_2 triangle layer and x-K layer. Compared with Na_xCoO_2, it contains Rh element that has stronger spin-orbit interaction and weaker electron–electron correlation than those of Co [8,9]. These differences lead to more complicated and versatile physical properties of K_xRhO_2 [8,9]. For example, it is theoretically proposed that there should have a giant thermoelectric performance in $K_{7/8}RhO_2$ system [10]. In experiment, $K_{0.49}RhO_2$ and $K_{0.63}RhO_2$ have relative large thermopower of 40 $\mu V\,K^{-1}$ and 46 $\mu V\,K^{-1}$ [9,11]. These values are larger than that in other normal metals, but are smaller than that of $NaCo_2O_4$ ($\sim$100 $\mu V\,K^{-1}$) [1]. Though several works have been conducted in K_xRhO_2 system, it is still in a primary stage for studying the possible physical property of K_xRhO_2. Has K_xRhO_2 varied physical properties that are strongly dependent on potassium content? Does the superconductivity exist in K_xRhO_2 system? Obviously, obtaining K_xRhO_2 single crystals with different potassium content is the prerequisite to exploring these problems.

Here we synthesized a series of low potassium content K_xRhO_2 single crystals by the *Chemical Depotassiation method*, which has been successfully employed to obtain low Na concentrated Na_xCoO_2 [3,4]. By this method, we prepared K_xRhO_2 samples with variable potassium content. And an end-product of $K_{0.32}RhO_2$

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crystal with single phase was obtained. Moreover, the electrical properties, magnetoresistance and Hall effect substantiate that the $K_{0.32}RhO_2$ crystal is a multi-band metal, which can be described by Fermi liquid theory.

2. Experimental details

Potassium rhodate crystals were grown by self-flux method, which was reported elsewhere [11–13]. As shown in Fig. 1(b), the metallic luster $K_{0.62}RhO_2$ crystal with size as large as $8 \times 5 \times 0.05$ mm^3 is obtained. To get low K content potassium rhodate crystals, the saturated I_2 acetonitrile solutions are used as oxidizing agent for the chemical depotassiation process. Then the grown $K_{0.62}RhO_2$ crystals were chosen carefully and cut as square shape with dimensionalities as $5 \times 5 \times 0.05$ mm^3. The temperature of solution was set at 25 °C. The chosen samples were dipped in the solution for fifteen minutes, and then got out to measure K content by the energy dispersive spectroscopy (EDS) in a scanning electron microscope (SEM, FEI-Quantum). Then the same samples were dipped in the solution again to extract potassium further. The same procedure was repeated for many times.

Single crystal XRD was carried out by an X-ray diffractometer (Philips PW 1710) using Cu Kα radiation. The electrical, magnetoresistance and Hall measured in a physical property measurement system (PPMS, Quantum Design) by means of six-electrode method.

3. Results and discussion

Fig. 2(a) shows the logarithm time dependence of potassium contents of the K_xRhO_2 crystals. Three samples (S1, S2 and S3) were characterized to reveal the universal law in the depotassiation process. The chemical reaction of depotassiation can be described as:

$$K_xRhO_2 + y/2I_2 \rightarrow K_{x-y}RhO_2 + yK^+ + yI^- \quad (1)$$

when the reaction time is below about 20,000 s, this relationship can be well fitted as

$$x = -0.04 \ln t + 0.62 \quad (2)$$

when the reaction time is beyond about 20,000 s, the value of x is saturated to 0.32. It is worth noting that the process is influenced by the shape, size and thickness of the initial samples and the

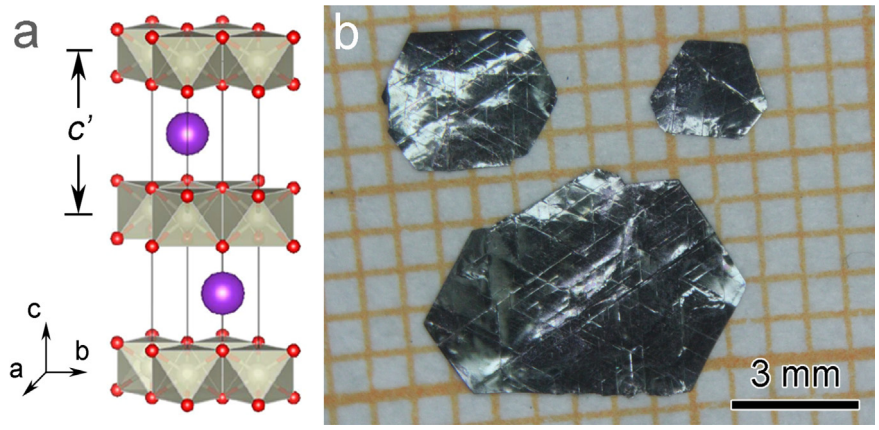

Fig. 1. (Color Online) (a) The schematic of atomic structure of K_xRhO_2. (b) The photo of the as-grown $K_{0.62}RhO_2$ crystal.

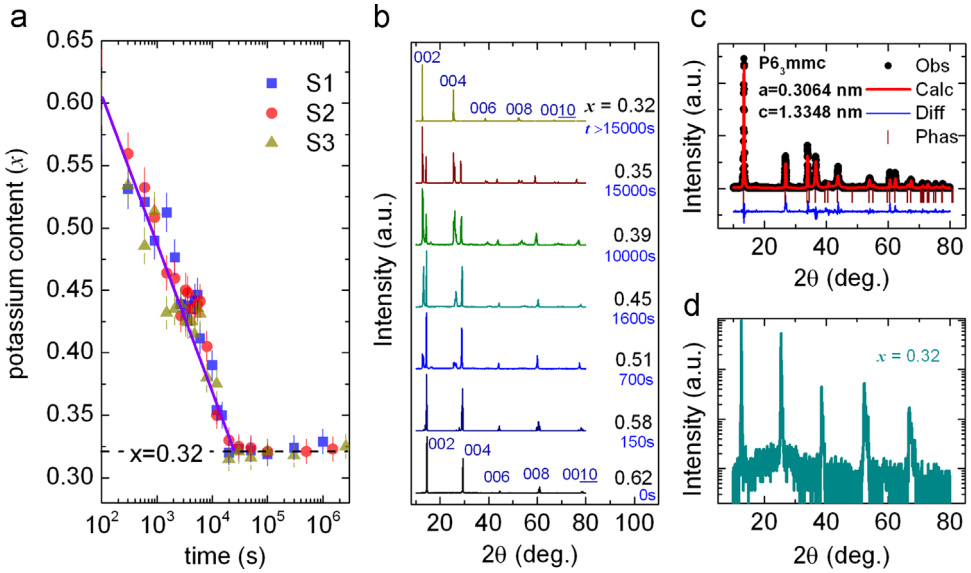

Fig. 2. (Color Online) (a) The logarithm time dependence of potassium contents are shown for samples 1, 2 and 3. And the relationship between potassium contents and time is fitted by the formula $x = -0.04 \ln t + 0.62$ when the reaction time is below about 20,000 seconds. While the value of x is saturated at a constant value 0.32 when the reaction time is beyond around 20,000 s. (b) The XRD of single crystalline samples with x varied from 0.62 to 0.32. And the corresponding reaction time is changed from 0 s to 1500 s. (c) The powder X-ray diffraction refinement of $K_{0.32}RhO_2$ sample. (d) The XRD of single crystal $K_{0.32}RhO_2$ sample.