Synthesis and morphological stability in CrO$_2$ single crystals of a half-metallic ferromagnetic compound

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Abstract: Single crystals of a half-metallic ferromagnetic compound CrO$_2$ were synthesized using controlled thermal evaporation of CrO$_3$ in an autoclave at 1.5 bar pressure at moderate temperature 673 K. These CrO$_2$ crystals lay in a Rutile tetragonal crystal structure of D$^{14}_{4h}$ space group, with lattice parameters $a = 0.4423$ nm and $c = 0.2918$ nm. The lattice volume 0.0571 nm$^3$ determines 4.88 g/cm$^3$ density, assuming a lattice consisting of two CrO$_2$ formula units. Scanning electron microscopic images reveal rectangular bars of single CrO$_2$ crystals of 6.0-8.0 µm lengths and 1.0-1.5 µm widths. When heating in ambient air pressure the crystals relieve part of the oxygen according to the CrO$_2$ $\rightarrow$ Cr$_2$O$_3$ phase transformation with a sharp peak in the first derivative of the thermogravimetric curve at temperature as early as 570 K, with a partial mass loss of 1.2%. A complete transformation appears around 775 K, with 3.0% mass loss. The CrO$_2$ $\rightarrow$ Cr$_2$O$_3$ conversion reflects in a sharp endothermic peak in DTA at 576 K. The CrO$_2$ crystals have the saturation magnetization of 68 emu/g, coercivity ~340 Oe, and remanent magnetization ~ 61 emu/g at room temperature.

1. Introduction

Chromium dioxide (CrO$_2$) of a Rutile tetragonal structure, with lattice parameters intermediate between those of the neighbouring Rutile oxides TiO$_2$ and MnO$_2$, is widely used as a ferromagnetic compound for magnetic recording tapes, Spin polarizer, giant magnetoresistance (GMR), and spintronic devices [1-5]. The ferromagnetism involves the complete spin polarization of the 3d conduction electrons below the Curie temperature ~390 K to give a half-metallic ferromagnet with a majority-spin band, i.e., 2/3 full and a minority-spin band, i.e., empty. Thus, CrO$_2$ has a saturation magnetization of 2.0 $\mu_B$ per Cr$^{3+}$ ion and exhibits the metallic conductivity expected for 2/3 filling of a spin-polarized band that can accommodate 3 electrons per cation [4–8]. The complete spin polarization of the conduction electrons is promising applications of granular GMR films for magnetoresistive and spintronic devices.

A disadvantage with CrO$_2$ is that it becomes thermodynamically unstable under ambient oxygen partial pressure at temperatures above 550 K. Thus, synthesizing a high quality stable CrO$_2$ compound

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by conventional high-temperature solid-state procedure is not possible at atmospheric pressure. Commercial synthesis routes for preparation of CrO$_2$ involve decomposition of precursor compounds under high oxygen partial pressure, usually assisted by hydrothermal conditions [9–11]. Recently, it has been reported that CrO$_2$ can be obtained by solid state reduction of CrO$_3$ with NH$_4$Br or NH$_4$I [12, 13]. However, a number of groups have achieved CVD-type growth of CrO$_2$ thin films under ambient oxygen pressures on Rutile TiO$_2$ and Al$_2$O$_3$ substrates using a precursor such as CrO$_3$ or CrO$_2$Cl$_2$ [14-20]. Here, we report a rather simple route of synthesis of surface stabilized CrO$_2$ of single crystals through a self-controlled thermal evaporation of CrO$_3$ in an autoclave reactor at moderate temperature and air pressure.

2. Experimental procedure

Chromium and its oxides may occur in several oxidation states, which include Cr$_2$(III)O$_3$, Cr(IV)O$_2$, Cr$_2$(V)O$_5$, and Cr(VI)O$_3$, respectively. Among these oxidation states, only Cr(IV) one is strongly ferromagnetic at room temperature. Unfortunately, it is difficult to stabilize because of metastable nature in ambient atmosphere. This pressure dependence synthesis of CrO$_2$ offers CrO$_3$ a most suitable precourser [21-23]. Here, we synthesized CrO$_2$ in form of single crystals by a thermal evaporation of CrO$_3$ in an AISI 316 stainless steel made autoclave reactor of typical dimensions 15 cm diameter and 30 cm height. In a typical batch of synthesis, about 20 mg of CrO$_3$ powder was placed in the autoclave reactor in a closed vessel of 25 ml volume. The autoclave reactor was heated at a rate of 280 K/min from room temperature and then held for 3 h at 525 K. At this temperature, CrO$_3$ relieves part of oxygen very slowly according to the instantaneous pressure (that is found to be nearly 0.5 bars at the transformation temperature 525 K) and ultimately converts into CrO$_2$, which is growing as single crystals.

The temperature-pressure analysis (TPA) provides quantitatively the conversion temperature and the pressure. It is observed that, at a specific pressure of ~ 0.5 bars, CrO$_3$ starts converting to CrO$_2$ at 525 K, adding the final pressure to be around 0.8 bars at 575 K. At this specific pressure of 0.8 bars, the sample temperature starts to be decreasing effectively, assuming as small value as 550 K. After ten min of the processing, both the temperature and pressure start again to be increasing assuming the equilibrium values 675 K and 1.5 bars, respectively. If the heating is stopped, the pressure continues to be increasing indicating the role of the temperature dependent kinetics. Around 775 K, the CrO$_2$ → Cr$_2$O$_3$ conversion reaches the completion. A plateau corresponds to the CrO$_2$ formation over 575-675 K. On running for the TPA at 2.0 bars CrO$_2$ decomposes at 730 K. The TPA data suggests that heating up to 675 K at 1.5 bars of pressure leads to CrO$_3$ → CrO$_2$ + ½ O$_2$ transformation.

The CrO$_2$ crystal structure was analyzed in terms of high resolution X-ray diffractogram (HXRD) and that was recorded using the Philips X‘pert Pro model PANalytical-3040 diffractometer, with filtered 0.17890 nm CoKα radiation. A high resolution scanning electron microscope (HRSEM) of Oxford model Leo1550 was used to obtain size and shape of the CrO$_2$ crystals. The magnetic properties were measured with a vibrating sample magnetometer of Lake Shore model-7407. A thermal analyzer of Perkin-Elmer model DT-40, Shimadzu Co. Japan, was used for studying thermogravimetric (TG) curve, its derivative curve (DTG), and DTA (differential thermal analysis) curve. The data were recorded by heating 20 mg sample in an aluminum pan at 5 K/min in N$_2$ gas.

3. Results and Discussions

3.1. Phase formation and microstructure of CrO$_2$ crystals

The HXRD pattern of the CrO$_2$ single crystals in the diffraction angle 2θ range of 25-115° is shown in figure 1. It consists of total twelve peaks which are indexed in terms of the (hkl) values in the tetragonal Rutile structure of space group P4$_2$/mnm. The lattice parameters $a = 0.4423$ nm and $c = 0.2918$ nm determined from the d$_{hlk}$ values (interplanar spacings) are similar to the reported $a = 0.4422$ nm and $c = 0.2917$ nm values on bulk CrO$_2$ [24]. The unit cell volume $V_0 = 0.0571$ nm$^3$ provides a
density $\rho = 4.88 \text{ g/cm}^3$, i.e., a reasonably lower value in comparison to $4.90 \text{ g/cm}^3$ in bulk CrO$_2$ ($V = 0.0569 \text{ nm}^3$), assuming $z = 2$ CrO$_2$ units [24]. Small CrO$_2$ crystals achieved in the present work accompany a thin Cr$_2$O$_3$ surface layer and that possibly tunes a lower $\rho$-value. Also the intensity distribution in the characteristic CrO$_2$ peaks differs markedly from the reported pattern in bulk CrO$_2$. For example, the most intense peak (peak intensity $I_p = 100$ units) arises in the (110) reflection along with the second and third most intense peaks in the (101) and (220) reflections of $I_p = 60$ and = 42 units, respectively. The $d_{\text{hkl}}$ values were 0.3130, 0.1444, and 0.2429 nm, respectively. The three most intense peaks in bulk CrO$_2$ arise in a different group of (110), (101) and (211) reflections in $I_p = 100$, 53, and 43 at 0.3124, 0.2434 and 0.1634 nm of $d_{\text{hkl}}$ values, respectively.

Figure 1. HXRD pattern in small CrO$_2$ crystals.

Figure 2 shows typical HRSEM images of the single CrO$_2$ crystallites of well-defined rectangular bars or platelets, with $L = 6.0-8.0 \mu\text{m}$ lengths, $W = 1.0-1.5 \mu\text{m}$ widths, and $\delta = 0.5-1.0 \mu\text{m}$ thickness. A value $\delta \leq W$ retains in preponderant local CrO$_3 \rightarrow$ CrO$_2 + \frac{1}{2} \text{O}_2$ transformation and reconstructive reaction. In such example, the $\delta$ value represents the effective crystallite size. Furthermore, the magnetic hysteresis loop measured with magnetic field up to 10 kOe (figure is not given here) shows the saturation magnetization $M_s = 68 \text{ emu/g}$, coercivity $H_c = 340 \text{ Oe}$, and remanent magnetization $M_r = 61 \text{ emu/g}$ at room temperature. A low $M_s$ value in comparison to a reported value 80 emu/g in a polycrystalline bulk CrO$_2$ [3.4] might be due to a presumably antiferromagnetic Cr$_2$O$_3$ surface layer.

3.2. Thermal analysis of CrO$_2$ crystals

Figure 3 shows (a) TG, (b) DTG, and (c) DTA thermograms of the CrO$_2$ crystals in a temperature range of 425-775 K. The data were measured during heating the sample under identical experimental conditions in the presence of N$_2$ atmosphere at a constant heating rate 5 K/min. The TG curve (in figure 3a) yields a total mass loss ($\Delta M$) of ~ 3.0 % against the initial mass of the sample in three successive steps as marked in the curve by the symbols I, II and III. In figure 3b, the DTG shows a sharp peak at 570 K, which follows a well-defined sharp peak at 576 K in correlation to the DTA in figure 3c. The DTA of the CrO$_2$ in figure 3c represents a rather sharp endothermic peak at 576 K, with
ΔM ≈ 2.5 % (in the regions I and II in figure 3a), which indicates a part of further decomposition of the CrO₂ in N₂ atmosphere. Moreover, the continuous heating of the CrO₂ results in a transformation into a Cr₂O₃ surface layer as reflected in the sharp endothermic DTA signal at 576 K. It admits the reported results over the CrO₂ → Cr₂O₃ transformation [21-23]. The region III infers residual CrO₂ → Cr₂O₃ conversion (adding ~ 0.5 % mass loss against a value 3.0 % in the complete transformation) over extended temperatures above the critical value 576 K in the sharp DTA or DTG peak.

Figure 2. HRSEM images showing small single CrO₂ crystallites of a submicrometer scale.

As demonstrated with the literature, a pure CrO₂ free from any surface modification starts to loose part of the oxygen at much lower temperature such as ~ 475 K in ambient air atmosphere [22]. Therefore, the mass loss in bulk CrO₂ mainly attributes to a heat induced thermal decomposition of CrO₂, i.e., a topotactic transformation from the Rutile CrO₂ phase to the corundum Cr₂O₃ phase. As
described elsewhere [21, 23], the crystallographic relations between the two phases are as follows; \{001\}Cr2O3 plane || \{100\}CrO2 plane and \{100\}Cr2O3 plane || \{001\}CrO2 plane. The present experimental results are useful in understanding the thermodynamic stability of small CrO2 crystals and in particular the process of its phase transformation to Cr2O3 as the equilibrium structure among the various possible chromium oxides, viz., CrO3, Cr2O5, CrO2, Cr2O3, CrO, or Cr2O [5, 15,21-23].

4. Conclusions

A self-controlled reconstructive CrO3 → CrO2 + 1/2 O2 transformation reaction is developed in an attempt to synthesize a half-metallic ferromagnetic CrO2 compound of small single crystals at moderate temperature. High quality CrO2 crystals of well-developed faces form in the usual Rutile tetragonal crystal structure (D14d;P42/mnm space group) under a small pressure such as 1.5 bars at temperature as high as 673 K in an autoclave reactor. The lattice parameters \(a = 0.4423\) nm and \(c = 0.2918\) nm determined from the X-ray diffraction pattern yields a density 4.88 g/cm³ (according to the lattice volume 0.0571 nm³ ) assuming a primitive cell of two formula units of CrO2. The electron microscopic images characterize rectangular bars or platelets of 6.0-8.0 µm lengths, 1.0-1.5 µm widths, and 0.5-1.0 µm thickness of single CrO2 crystallites. The stable sample in ambient atmospheres converts to Cr2O3 very slowly and only when heating above 450 K, showing a three step mass loss with a total of 3.0% in a thermogravimetric analysis. A sharp endothermic peak in DTA at 576 K corroborates the result of the CrO2 → Cr2O3. At room temperature, the CrO2 crystals are ferromagnetic with ~ 68 emu/g saturation magnetization, ~ 340 Oe coercivity, and ~ 61 emu/g remanent magnetization.

5. References

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