A new method for the synthesis of chromium(IV) oxide at ambient pressure†

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The reaction $CrO_3 + 2NH_4X \rightarrow CrO_2 + 2\ NH_3 + H_2O + X_2$ (X = Br, I), which occurs quantitatively at 120–150 °C, provides a convenient method for the synthesis of CrO_2; unlike conventional methods, the method reported here does not require the use of high pressure for the synthesis of this technologically important material.

Chromium(IV) oxide, CrO_2, is unique among the rutile-type transition metal dioxides,[1] exhibiting ferromagnetic (T_c = 395 K) and metallic properties.[2] Because of these properties, the material finds application as a magnetic recording medium in the form of tapes. In recent years, there has been a renewed interest in this material in view of the realization[3] that it is a ‘half-metallic’ ferromagnet [*i.e.*, the majority (spin-up) electrons are delocalized, while the minority (spin-down) electrons are localized, having a semiconductor-like gap in the density-of-states] with a nearly 100% spin polarization[4] at the Fermi energy. An important consequence of the half-metallic nature is that films of CrO_2 exhibit a low-field tunneling-type magnetoresistance[5] that appears promising for application.

Since CrO_2 is a metastable phase[2] (decomposing at > 288 °C at 1 atm pressure of O_2), all the methods reported for its synthesis require high pressures.[2] Hydrothermal decomposition of aqueous solutions of CrO_3 at elevated temperatures and pressures (typically 480 °C and 2 kbar) is a common method for the synthesis of polycrystalline CrO_2 powders.[2] Growth of single crystals[6] however require much higher temperatures (900–1300 °C) and pressures (60–65 kbar).

Considering the technological and scientific importance of CrO_2, we developed a new method for its synthesis at ambient pressure. Our method is based on the low-temperature (120–150 °C) reduction of CrO_3 by NH_4I/NH_4Br followed by annealing the solid product at temperatures below the decomposition point of CrO_2. The method crucially depends on the solid state reaction given by eqn. (1)

$$CrO_3 + 2\ NH_4X \rightarrow CrO_2 + 2\ NH_3 + X_2 + H_2O \qquad (1)$$

which occurs quantitatively between 120 and 150 °C. Here, we describe the details of synthesis of crystalline CrO_2 by this method and its characterization.

Stoichiometric quantities of CrO_3 (20 mmol) and NH_4X (X = Br, I) (40 mmol) corresponding to eqn. (1) were thoroughly mixed under CCl_4. The mixture, taken in a Pyrex glass tube connected to a vacuum line, was heated slowly *in vacuo* (*ca.* 10^{-5} Torr) under continuous pumping conditions as described earlier.[7] Copious evolution of I_2/Br_2 occurred around 120 °C. The temperature was raised to 150 °C and held at this value until the evolution of I_2/Br_2 ceased (2–3 h). The liberated I_2/Br_2 condensed in a liquid nitrogen trap provided a quantitative measure of the extent of the reduction.[7] Significantly, reaction (1) does not occur with NH_4Cl. This is consistent with the redox characteristics of Cr^{VI} which oxidizes I^- and $Br-$ but not Cl^- in aqueous solutions.[8]

The black solid product of reaction (1) was stable in air; it was however non-magnetic and amorphous to X-rays [Fig. 1(a)]. Pellets of this product were annealed in evacuated sealed glass tubes at various temperatures and times. We found that annealing at 195 ± 5 °C for one week yielded crystalline CrO_2 with rutile structure. The lattice parameters, a = 4.419 (1), c = 2.915 (1) Å, derived from the X-ray powder diffraction pattern [Fig. 1(b)] are in excellent agreement with the values reported for CrO_2 in the literature.[9] Determination of oxygen content by iodometric titration revealed that the product is stoichiometric ($CrO_{1.99 \pm 0.02}$).

Measurement of electrical resistivity and magnetic susceptibility revealed that the CrO_2 prepared here is metallic and ferromagnetic as expected. The resistivity and susceptibility data of our samples (Fig. 2) are comparable to the corresponding data reported in the literature[5] for bulk polycrystalline samples

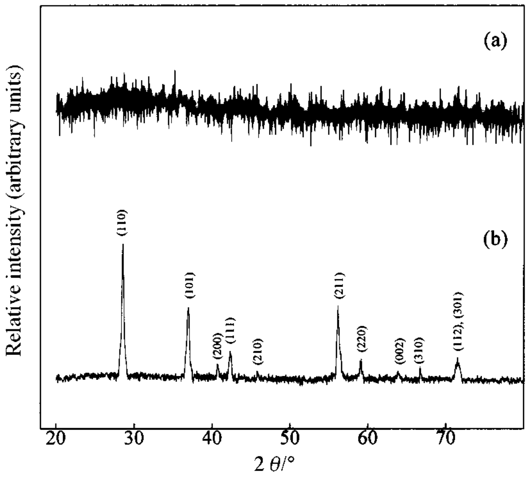

Fig. 1 Powder XRD patterns (Cu-Kα) of (a) solid product of reaction (1) with NH_4I and (b) product (a) annealed at 195 ± 5 °C for one week corresponding to crystalline CrO_2.

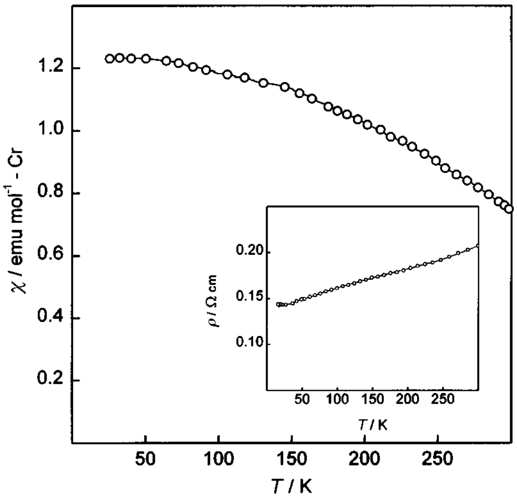

Fig. 2 Temperature dependence of magnetic susceptibility of CrO_2 measured at 0.5 T. Inset shows the temperature dependence of electrical resistivity of the same sample.

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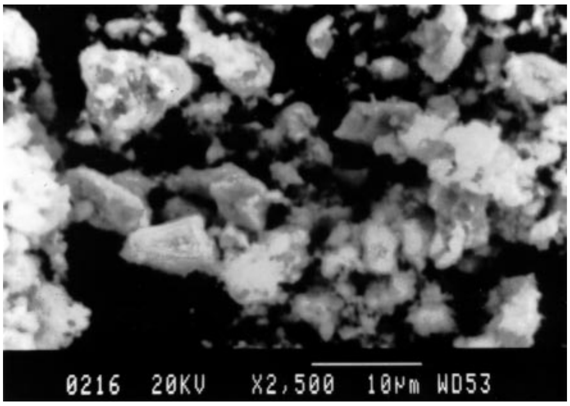

Fig. 3 SEM image of crystalline CrO_2.

as well as films of CrO_2. An SEM study showed that the samples are fairly crystalline, the particle sizes being in the range of a few µm (Fig. 3).

We believe that the key to the success of the method lies in the quantitative nature of reaction (1) which can be controlled to give an average oxidation state of Cr^{IV} in the solid state by using the required quantity of NH_4I/NH_4Br in the reaction mixture. This is in contrast to reactions between Cr^{VI} and I^-/Br^- in aqueous media, which proceed directly to give Cr^{III}; *i.e.* Cr^{VI} is not accessible as a stable species in aqueous media by redox reactions. An investigation of the X-ray morphous CrO_2 would throw light on the mechanism of reaction (1) which stabilizes Cr^{VI} in the solid state.

We can also prepare rutile-related (monoclinic) VO_2 as well as solid solutions of $Cr_{1-x}V_xO_2$ by the same method starting from V_2O_5 and V_2O_5–CrO_3 mixtures. Therefore, we believe that the method described here can be extended to the synthesis of other metastable oxides containing Cr^{IV} and/or V^{IV}, in general.

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