

# Magnetic Properties of $V_2O_3$ Nanooxide Prepared Mechanochemically With and Without Salt Matrix

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We present a new technological route of synthesis of  $V_2O_3$  nanocrystals based on mechanochemical reduction of  $V_2O_5$  with  $Na_2SO_3$  as a reductant, followed by low temperature vacuum annealing. The structural and magnetic properties of the  $V_2O_3$  nanocrystals were studied.

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## 1. Introduction

$V_2O_3$  has been extensively studied as the canonical Mott-Hubbard system.  $V_2O_3$  bulk shows the first-order metal-insulator transition at about 150–170 K, with an accompanying seven-order magnitude increase in conductivity and a shift from an antiferromagnetic to paramagnetic behaviour.

Bulk  $V_2O_3$  has been traditionally prepared by a reduction of  $V_2O_5$  with  $H_2$  at a high temperature; however, calcination temperature  $> 800^\circ C$  is often needed to obtain the required  $V_2O_3$  phase. On the other hand, high temperatures result in particle coarsening and agglomeration. Mechanochemical synthesis by a high-energy ball milling process is an alternative to calcination at elevated temperatures. This processing involves the preparation of nanopowders embedded in a salt matrix, which is formed as the second reaction product [2].

## 2. Experimental

Anhydrous  $Na_2SO_3$  p.a. and  $V_2O_5$  powder obtained by thermal decomposition of  $NH_4VO_3$  p.a. at  $500^\circ C$  were used as starting reactants. Mechanochemical reduction between  $V_2O_5$  and  $Na_2SO_3$  was performed in a high-energy planetary ball mill TB-2 at 890 rpm. 10 g of the starting mixture corresponding to the  $V_2O_5/Na_2SO_3$  molar ratio of 1:2.5 was loaded into corundum jars of  $0.2\text{ dm}^3$  inner volume, together with 10 mm diameter  $ZrO_2$  ceramic balls (YTZ, Tosoh, Japan). The milling was performed under air atmosphere for 10 min. The ball-to-powder mass ratio was 20:1.

The A-sample including the salt matrix  $Na_2SO_4$  was prepared from 10 min milled starting composition, followed with annealing in the vacuum chamber at  $550^\circ C$  for 1 hour. The B-sample was prepared likewise the A-sample, however, it was annealed at  $450^\circ C$  and its salt

matrix was removed by washing with water. X-ray powder diffraction was carried out using a Philips PW 1050 diffractometer (Cu  $K_\alpha$  radiation). The milled powders were annealed at different temperatures in the vacuum chamber for 1 hour; finally washed. Temperature dependences of the zero-field cooled (ZFC) and field cooled (FC) DC magnetic moment and magnetization  $M(H)$  curves were measured by the QD SQUID magnetometer MPMS XL-7. Molar (per V atom) susceptibilities  $\chi'$  of the samples were corrected for the effect of the sample holder and for the diamagnetic contribution, evaluated using the tabulated values of diamagnetic susceptibilities of cations and anions given by Bain and Berry [1]. ZFC curves were fitted by the Curie-Weiss law,  $\chi = C/(T - \Theta)$  and values of the Curie constant  $C$ , Weiss temperature  $\Theta$  and effective magnetic moment  $\mu_{eff}$  were estimated.

## 3. Results and discussion

Figure 1a shows the XRD patterns of the starting  $V_2O_5/Na_2SO_3$  mixture with the molar ratio of 1:2.5. After 10 min milling, Fig. 1b, very broad peaks corresponding to the low-crystalline nonstoichiometric  $VO_2$ , as always visible [2], were observed.

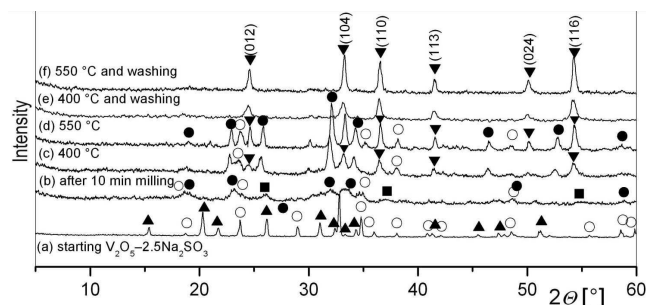


Fig. 1. XRD patterns of the starting  $V_2O_5-2.5Na_2SO_3$  mixture (a), milled for 10 min (b), vacuum treatment at 400 and  $550^\circ C$  (c, d),  $V_2O_3$  nanocrystals obtained after washing procedure, (e, f). (▲):  $V_2O_5$ ; (■):  $VO_2$ ; (▼):  $V_2O_3$ ; (○):  $Na_2SO_3$ ; (●):  $Na_2SO_4$ .

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The effect of vacuum annealing at 400–550 °C on the phase composition is shown in Fig. 1c, 1d. After annealing, the whole  $VO_2$  was reduced to  $V_2O_3$ , (Fig. 1c, 1d). After the removal of the salt matrix by washing, for the samples annealed at 400–550 °C, all the diffraction peaks are in close agreement with rhombohedral  $V_2O_3$  (JCPDS file No. 34–187). The average crystallite size calculated from the (012) diffraction peak broadening by the application of the Scherrer formula was  $\sim 20$ –55 nm, which is in agreement with the TEM observation, that also supports the existence of a well-developed morphology of  $V_2O_3$  nanoparticles [5].

ZFC and FC molar susceptibility  $\chi'$  vs.  $T$  dependences of A-sample are shown in Fig. 2.

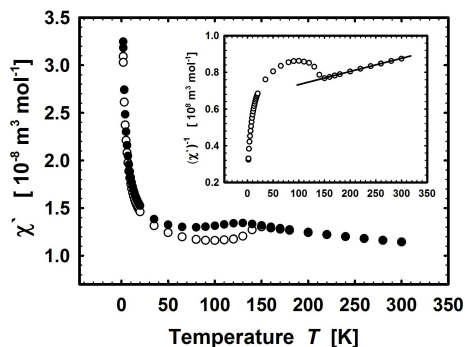


Fig. 2. Molar susceptibility  $\chi'$  vs.  $T$  of the A-sample at  $1.6 \text{ kA m}^{-1}$ ; ZFC ( $\circ$ ), FC ( $\bullet$ ). The inset shows the inverse molar susceptibility  $(\chi')^{-1}$  vs.  $T$ . The solid line is the fit of the Curie-Weiss law.

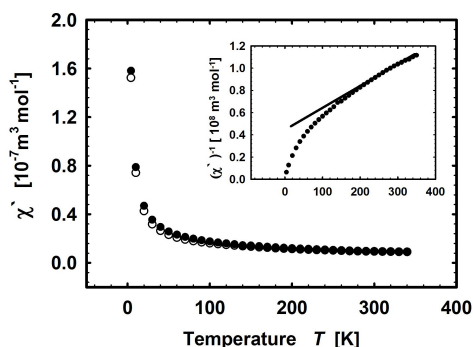


Fig. 3. As Fig. 2 for B-sample at  $4 \text{ kA m}^{-1}$ ; ZFC ( $\circ$ ), FC ( $\bullet$ ).

The ZFC-FC hysteresis effect is seen from  $\sim 50$  to 145 K and magnetic transition from the AFM to PM state is seen at  $T_t = 144 \text{ K}$ . The value of  $T_t$  is in line with those reported for the insulator-metal transition of  $V_2O_3$  powders (nanowires, nanocrystals), namely, if a light non-stoichiometry is considered [3, 4]. Moreover, the magnetization curves observed at temperatures of  $T = 10$ –300 K were linear and non-hysteretic.

Figure 3 shows  $\chi'$  vs.  $T$  of the B-sample. In contrast to the A-sample, the B-sample shows neither apparent ZFC-FC hysteresis, nor susceptibility peak determining the transition temperature  $T_t$ . The linear and practically zero coercivity magnetization curves  $M(H)$  at 20 and

300 K for the B-sample are shown in Fig. 4.

The values of  $\mu_{eff}$  and  $\Theta$  for the A (B)-sample 3.03 ( $3.01$ )  $\mu_B$  and  $-962$  ( $-917$ ) K, respectively, were obtained from fitting the high-temperature data (Inserts in Fig. 2 and 3) to the Curie-Weiss law.

The differences in the  $\chi'$  vs.  $T$  dependences of the A and B samples could be ascribed to effects of diamagnetic salt matrix, water washing and air exposure on surface properties of nanoparticles, rather than to the different average crystallite size or particle size distribution of the A- and B-samples.

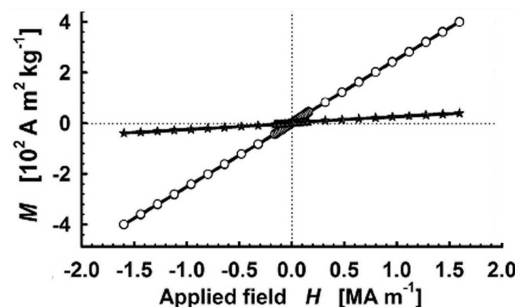


Fig. 4.  $M$  vs.  $H$  of the B-sample at 20 ( $\circ$ ) and 300 K ( $\star$ ).

#### 4. Conclusions

The  $V_2O_3$  nanoparticles (20–50 nm) were prepared via mechanochemical reduction of  $V_2O_5$  with  $Na_2SO_3$  as a reductant, followed by low temperature vacuum annealing. For the sample annealed at 550 °C, containing both  $V_2O_3$  and the diamagnetic matrix  $Na_2SO_4$ , paramagnetic to antiferromagnetic transition at  $T_t = 144 \text{ K}$  was observed, whereas the sample annealed at 450 °C after the salt matrix removal shows no evident value of  $T_t$ .

The values of the Weiss temperature  $\Theta$  and the effective magnetic moment  $\mu_{eff}$  of the samples after diamagnetic corrections were estimated to be  $-962 \text{ K}$  ( $-917 \text{ K}$ ) and  $3.03\mu_B$  ( $3.01\mu_B$ ) for samples with (without) salt matrix.

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