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Nanoparticles of superconducting γ-Mo_2N and δ-MoN

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Abstract

We have been able to prepare nanoparticles (~4 nm diameter) of cubic γ-Mo_2N by a simple procedure involving the reaction of $MoCl_5$ with urea at 873 K. The nanoparticles show a superconducting transition around 6.5 K. The γ-Mo_2N nanoparticles are readily transformed to nanoparticles of δ-MoN with a slightly larger diameter on heating in a NH_3 atmosphere at 573 K. Phase-pure δ-MoN obtained by this means shows a superconducting transition around 5 K.

Keywords: Nitrides; Nanoparticles

1. Introduction

Molybdenum nitride phases known to-date include the stoichiometric, hexagonal compound δ-MoN, and two nonstoichiometric compounds, cubic γ-Mo_2N and tetragonal β-Mo_2N. δ-MoN is a hard material with a low compressibility, showing a superconducting transition in the 4–12 K range [1,2]. γ-Mo_2N is also known to be a superconductor with a T_c of 5.2 K [3]. A theoretical study has predicted that γ-MoN with a cubic NaCl type structure would have a superconducting T_c as high as 29 K [4]. Various methods have been used to synthesize molybdenum nitrides. Plasma spraying molybdenum powder with an argon–nitrogen mixture is reported to result in a mixture of molybdenum nitride phases [5]. Jaggers et al. [6] report the synthesis of γ-Mo_2N and δ-MoN by the reaction between molybdates and NH_3. Lengauer [7] has investigated the formation of γ-Mo_2N and δ-MoN by the reaction between $MoCl_5$ and ammonia while Bull et al. [2] obtained phase-pure δ-MoN by this reaction carried out at 933 K. γ-Mo_2N has been prepared by heating the $MoCl_5$–hydrazine complex [8] and by refluxing a mixture of Na_2MoO_4, $(Me_3–Si)_2NH$, Me_3SiCl and NEt_3 in 1,2-dimethoxyethane [9]. Hansen et al. [10] report the synthesis of γ-Mo_2N and δ-MoN by the decomposition of an imidomolybdenum complex. γ-Mo_2N can also be prepared by the metathesis reaction between $MoCl_5$ and Ca_3N_2 [11]. Marchand et al. [12] obtained powders of δ-MoN and Mo_5N_6 by the ammonolysis of MoS_2. Thermal decomposition of pyrazolyl and hexamethylenetetramine complexes of molybdenum yields γ-Mo_2N [13,14]. Nanocrystalline γ-Mo_2N and δ-MoN with T_c values of 3.8 and 7.5 K, respectively, have been prepared by heating hydroxylamine complexes of molybdenum in NH_3 [15]. Inumaru et al. [16] have recently prepared γ-Mo_2N by heating $MoCl_5$ under a flow of mixed gas of N_2 and H_2 and β-Mo_2N films by the pulsed laser deposition of molybdenum metal under nitrogen radical irradiation.

We have developed a very simple method to prepare γ-Mo_2N and δ-MoN by employing the urea route based on the reaction of metal halides with urea. It is to be noted that this methodology has been successively exploited to produce binary nitrides such as BN, TiN, and NbN [17]. By employing the reaction of $MoCl_5$ with urea we have obtained nanoparticles of γ-Mo_2N. By heating γ-Mo_2N in a NH_3 atmosphere, we were able to prepare stoichiometric δ-MoN. Both γ-Mo_2N and δ-MoN prepared by us are in nanoparticulate form, exhibiting superconductivity.

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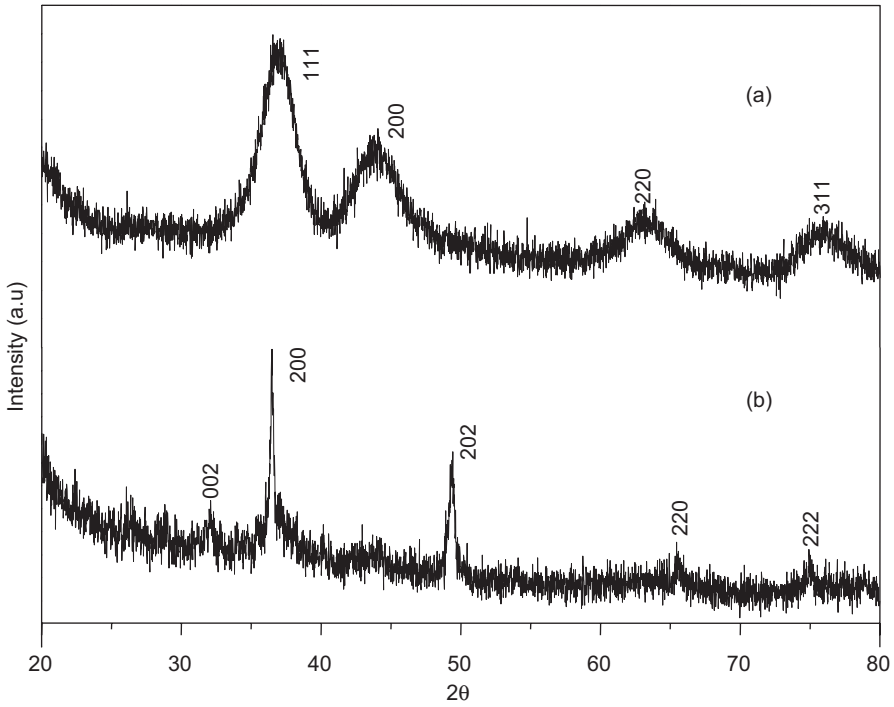

Fig. 1. XRD patterns of (a) γ-Mo_2N (b) δ-MoN recorded using Cu$K\alpha$ radiation.

2. Experimental

In the synthesis of γ-Mo_2N, a mixture of $MoCl_5$ and urea in the molar ratio of 1:12 was taken in an alumina boat and placed in quartz tube and heated at 873 K for 3 h in a N_2 atmosphere. Alternatively, an adduct of $MoCl_5$ and urea was prepared by taking the two compounds in the molar ratio of 1:12 in acetonitrile. The brown adduct so obtained was taken in an alumina boat and placed in quartz tube and heated at 873 K for 3 h in a N_2 atmosphere. The black product obtained at the end of the reaction was collected for further characterization. γ-Mo_2N was heated in NH_3 at 573 K for 72 h to prepare δ-MoN.

The products formed in the above reactions were characterized by various techniques. X-ray diffraction (XRD) patterns were recorded using Cu$K\alpha$ radiation on a Rich-Siefert XRD-3000-TT diffractometer. Thermogravimetric analysis (TGA) was carried out on a Mettler-Toledo-TG-850 instrument. Scanning electron microscope (SEM) images were obtained using a LEICA S440i SEM. Transmission electron microscope (TEM) images were obtained with a JEOL JEM 3010, operating with an accelerating voltage of 300 kV. Magnetic measurements were carried out with a vibrating sample magnetometer in Physical Property Measurements System (PPMS, Quantum Design).

3. Results and discussion

The product of heating the 1:12 mixture of $MoCl_5$ and urea at 873 K for 3 h gave the XRD pattern shown in Fig. 1a. The pattern is characteristic of cubic γ-Mo_2N (space group = $Pm3m$, $a = 4.1497$ Å, JCPDS card no: 25-1366). We estimate the particle size from the Scherrer formula to be ~6 nm. The TEM image shown in Fig. 2(a) shows the product of the $MoCl_5$-urea reaction to be an agglomerate of small particles of γ-Mo_2N. On sonication for 15 min, we obtained particles which were well-separated. We show a TEM image of these particles in Fig. 2(b). We find the average size of the nanoparticles of γ-Mo_2N from the TEM image to be 4.5 nm. The selected area electron diffraction (SAED) pattern shown as an inset in Fig. 2(b) reveals the single crystalline nature of the particles. The TGA curve of γ-Mo_2N carried out in an oxygen atmosphere (see curve a in Fig. 3) gave a mass loss corresponding to the formation of MoO_2. The initial increase in mass is due to the oxidation reaction. The stoichiometry of the nitride calculated from TGA is $MoN_{0.56}$. The XRD pattern of the product, shown as an inset in Fig. 3, confirms the product to be MoO_2.

In Fig. 4, we show the results of magnetic measurements on the nanoparticles of γ-Mo_2N under zero-field-cooled (ZFC) and field-cooled (FC) conditions (at 19.6 Oe). The data show a superconducting transition with an onset T_c around 6.5 K. Electrical resistivity measurements on the γ-Mo_2N nanoparticles (shown as an inset in Fig. 4) shows the superconducting transition with a T_c of around 7 K. The superconducting volume fraction is around 0.8%. It is noteworthy that the nanoparticles of γ-Mo_2N with an average size of 4.5 nm exhibit superconductivity.

In order to prepare δ-MoN, we heated the 4.5 nm nanoparticles of γ-Mo_2N in a NH_3 atmosphere for 72 h at

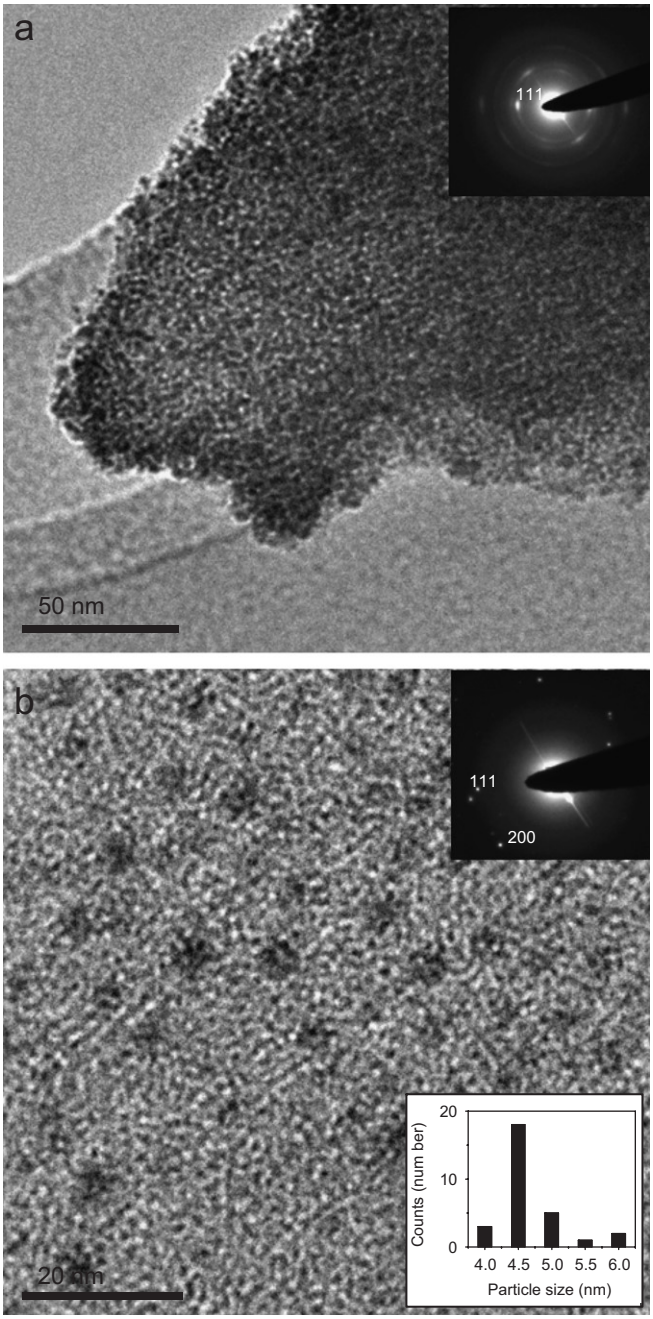

Fig. 2. (a) TEM image of the as-synthesized γ-Mo_2N particles and the inset shows the SAED pattern of the particles (b) TEM image of the γ-Mo_2N particles sonicated for 15 min with the inset showing the SAED pattern of a particle.

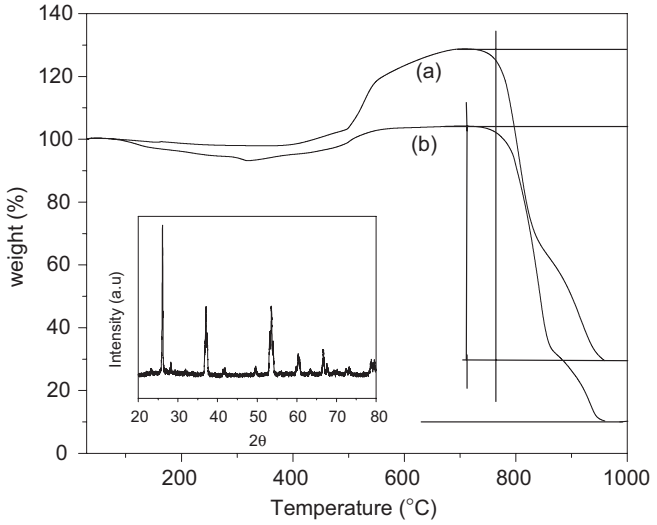

Fig. 3. TGA of (a) γ-Mo_2N (b) δ-MoN in oxygen atmosphere with inset showing the XRD pattern of the final product recorded using Cu$K\alpha$ radiation.

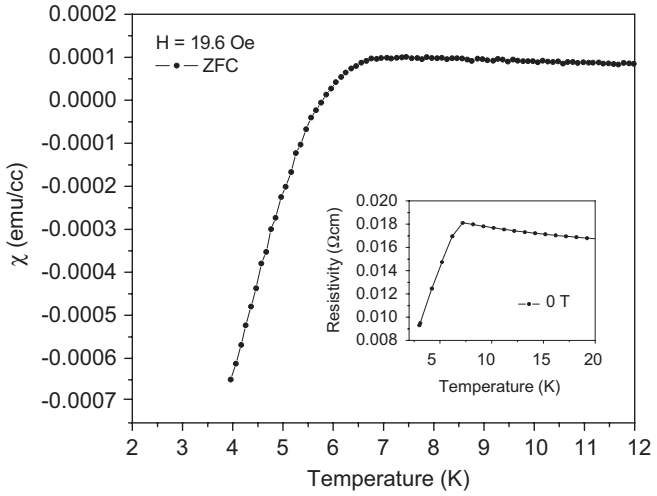

Fig. 4. Temperature dependence of magnetic susceptibility of γ-Mo_2N nanoparticles with the inset showing the resistivity of the sample as a function of temperature.

573 K. The product gave the XRD pattern characteristic of δ-MoN as shown in Fig. 1(b). It has a hexagonal structure of space group $P6_3/mmc$ with $a = 5.68$ Å, $c = 5.56$ Å (JCPDS card no: 25-1367). Based on the XRD line-widths, the particle size is estimated to be ~40 nm. Fig. 5(a) shows the TEM image of the δ-MoN nanoparticles. From the TEM image, we estimate the particle size to be in the 30–35 nm range. It appears that the γ-Mo_2N to δ-MoN transformation in an NH_3 atmosphere is accompanied by an increase in particle size. The high resolution electron microscope (HREM) image in Fig. 5(b) reveals the nanoparticles to be single crystalline. It is interesting that single crystalline γ-Mo_2N transforms to single crystalline δ-MoN. The TGA curve of δ-MoN carried out in an oxygen atmosphere is shown in Fig. 3(b). The TGA curve gave a mass loss corresponding to the formation of MoO_2 as confirmed by the XRD pattern of the product. Here again, the initial increase in mass is due to the oxidation reaction and the calculated stoichiometry of the nitride from TGA is $MoN_{0.95}$. We tried to prepare δ-MoN by the reaction of γ-Mo_2N with urea, but always ended with a slightly impure product. This is because when urea is decomposed at relatively low temperatures, there will be

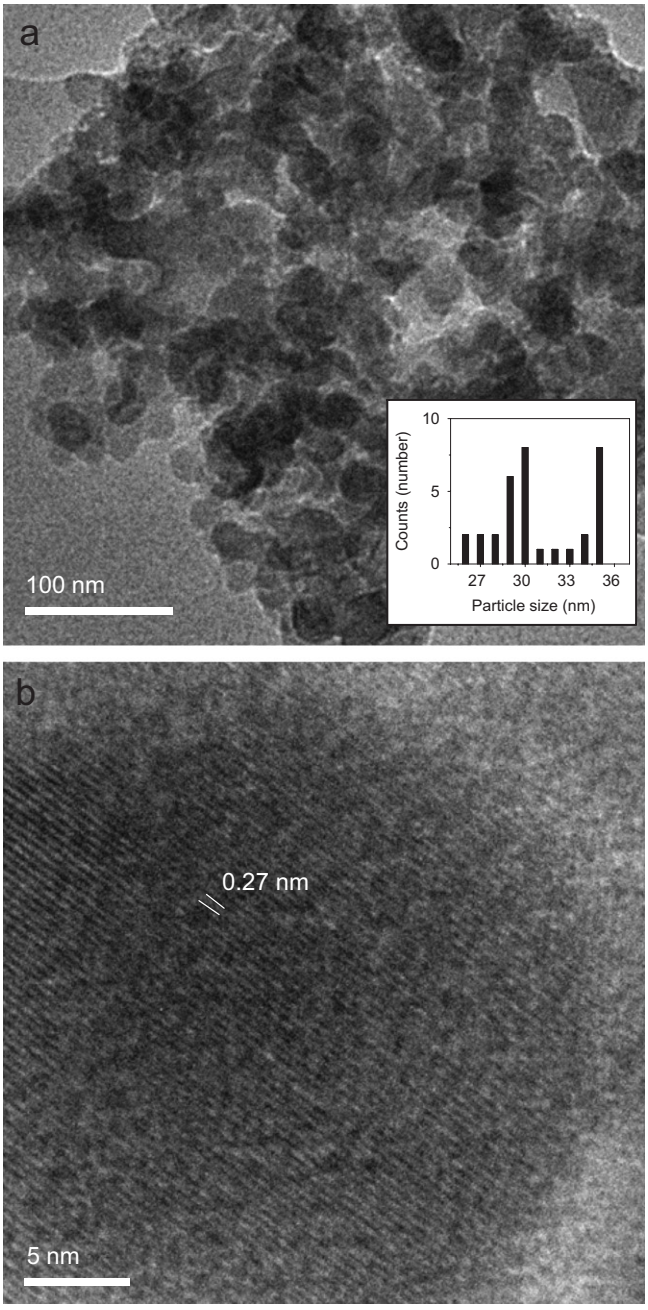

Fig. 5. (a) TEM image of the δ-MoN nanoparticles (b) HREM image of a δ-MoN particle.

other side-products in addition to one mole of NH_3 for one mole of urea. The side products can be eliminated at high temperatures but under those conditions δ-MoN is not stable.

In Fig. 6 we show the results of the magnetic measurements on δ-MoN. We see a superconducting transition around 5.6 K. The superconducting volume fraction is around 6.3%. It is known that the superconducting transition temperature of δ-MoN varies with the extent of disorder in the structure, the T_c of 4 K in highly disordered δ-MoN increasing to a value of 12.1 K in

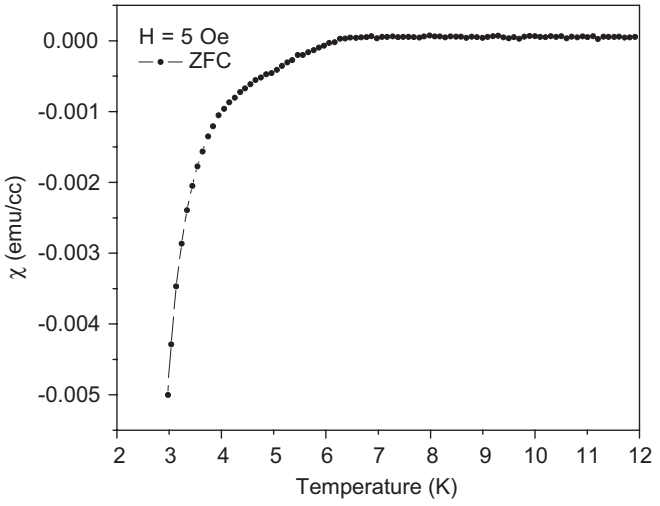

Fig. 6. Temperature dependence of magnetic susceptibility of δ-MoN nanoparticles.

the ordered phase [2]. The T_c observed by us is in between these values.

4. Conclusions

The reaction between urea and $MoCl_5$ is shown to readily give γ-Mo_2N under relatively mild conditions. In this reaction, urea decomposes to give NH_3 at temperatures greater than 500 K along with the cyanic acid which decomposes further to give products like biuret [18]. The NH_3 so produced reacts with $MoCl_5$ to give γ-Mo_2N. The procedure has enabled the synthesis of nanoparticles of superconducting γ-Mo_2N. It is also noteworthy that the γ-Mo_2N nanoparticles readily transform to δ-MoN nanoparticles on heating in NH_3 at a relatively low temperature. The δ-MoN so obtained seems to be somewhat disordered since the superconducting transition is around 5 K.

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