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# Preparation and magnetic characterization of ultrafine-grained ζ-$Mn_2N_{0.86}$ compound bulk

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ABSTRACT

The ultrafine-grained ζ-$Mn_2N_{0.86}$ compound bulk was prepared by a novel method that combined the solid-gas reaction, ball milling and spark plasma sintering. Characterizations on the magnetic properties showed that the Néel temperatures of the ball-milled powder and the ultrafine-grained bulk of $Mn_2N_{0.86}$ compound are drastically reduced as compared with the coarse-grained polycrystalline ζ-phase Mn-N compounds. Furthermore, it was found that the antiferromagnetism and the weak ferromagnetism coexist in the ball-milled powder and the ultrafine-grained bulk of $Mn_2N_{0.86}$ compound.



## 1. Introduction

As a special group of nitride compounds, the transition-metal nitrides have attracted increasing interests owing to its optical, electronic and magnetic performance, as well as the potential applications in the fields such as optical coatings, magnetic recording and sensing [1–4]. Among the transition-metal nitrides, manganese nitrides are more important due to the findings that some members in the manganese nitrides family exhibit specific magnetic performance [5]. As an example, it was firstly reported in *Science* [6] the possibility of forming a diluted magnetic nitride semiconductor (DMNS) with a high Curie temperature in a (Ga, Mn)N compound [7].

It is known that the manganese nitrides have different phases with unique structural and magnetic properties. The $Mn_4N$ (ε-phase) with the face-centered cubic (f.c.c.) structure is a ferrimagnetic compound having the Curie temperature of 738 K [8–10]. The $Mn_3N_2$ (η-phase) and MnN (θ-phase) with the face-centered tetragonal (f.c.t.) structure are antiferromagnetic compounds having the Néel temperature of 925 K and 650 K, respectively [11]. In the past decades, much attention was focused on the $Mn_4N$ compound due to its simple perovskite-derived structure, unique ferrimagnetic property, and the high Curie temperature. Recently, more efforts have been paid to studies on $Mn_3N_2$ and MnN compounds due to their antiferromagnetic properties and potential applications in the ferromagnetic/antiferromagnetic multilayers and magnetic/non-magnetic nitride semiconductor multilayers [5,12]. Although the $Mn_2N$, $Mn_5N_2$ and $Mn_2N_{0.86}$ are also antiferromagnetic compounds [13], which are ζ-phase with the hexagonal closely-packed (h.c.p.) structure, studies on the preparation and properties of this kind of manganese nitrides are very limited [13–16]. The main reason may be that the ζ-phase can exist stably only when the temperature is higher than 388 °C, which can be found from the Mn-N phase diagram [17]. However, a previous investigation [14] proposed that the ζ-phase could exist at the room temperature in the composition region with the concentration of nitrogen varying from 28at.% to 33at.%. Unfortunately, the preparation of the stoichiometric ζ-phase compound that is stable at room temperature, as well as the characterization of the magnetic properties of the ζ-phase compound bulk, has been very rarely reported in the literature.

In the present paper, we focus on the preparation and characterization of the ζ-$Mn_2N_{0.86}$ compound bulk, which has the nitrogen concentration of approximately 30at.%, nearly at the center of the ζ-phase composition region. We report here a novel method that combines the solid-gas reaction with the ball-milling to produce the single-phase $Mn_2N_{0.86}$ powder, then applies the spark plasma sintering (SPS) technique to fabricate the ζ-$Mn_2N_{0.86}$ compound bulk material with the ultrafine-grained structure. The microstructure and the magnetic properties of the prepared $Mn_2N_{0.86}$ bulk will be studied.

## 2. Experimental

The pure Mn powder (99.99%) with the mean particle size of 45 μm and the pure $N_2$ gas (99.999%) were used as the starting materials to synthesize the manganese nitrides powder by solid-gas reaction in the vacuum furnace (MTI GSL 1600X) at 1023 K for 5 h. Subsequently, the synthesized powder was ball-milled with a ball-to-powder ratio of 10:1, a rotation speed of 400 rpm, and a milling time of 20 h. The ball-milling process was performed in the argon atmosphere. The as-milled powder was fed into a high-strength graphite die then sent to the SPS equipment (SPS 3.20-MK-V). In the sintering process, a heating rate of 100 K/min was used till the temperature reached 973 K. An external pressure of

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60 MPa was applied to the powder through the upper and lower punches after 773 K. The holding time of 5 min was used at the sintering temperature. The SPS consolidation process was performed in the argon atmosphere to inhibit the decomposition of the manganese nitride during the sintering densification.

The phase constitutions of the solid-gas reaction product, the ball-milled powder and the SPSed bulk were detected by the X-ray diffraction (XRD) with Cu Kα radiation. The microstructure of the SPSed bulk was observed using the transmission electron microscopy (TEM, JEOL 3010) operated at 200 kV. The magnetic properties of the ball-milled powder and the SPSed bulk were measured by the superconducting quantum-interference device (SQUID) magnetometer at the maximum external field of 25 kOe, and also in a temperature range from 300 K down to 5 K for temperature dependence of magnetization with an external field of 500Oe.

## 3. Results and discussion

The XRD analyses on the phase constitution of the $Mn_2N_{0.86}$ compound at different preparation stages are shown in Fig. 1. As indicated by curve "a" in Fig. 1, the solid-gas reaction product is composed of the $Mn_2N_{0.86}$ compound as the dominant phase, with a little MnO which is hardly avoidable in the preparation processes of manganese nitrides as reported in literature [18]. The curve "b" in Fig. 1 demonstrates the phase analysis on the reaction product after ball milling. All the strong diffraction peaks are identified as the $Mn_2N_{0.86}$ phase. The "disappearance" of the MnO peaks is because of the overlapping with the broadened $Mn_2N_{0.86}$ peaks due to the formation of the ultrafine structure after milling. As a matter of fact, the small quantity of MnO still exists in the milled powder. A few greatly broadened peaks with very low diffraction intensities indicate the formation of the amorphous structure in part of the milled powder. The curve "c" in Fig. 1 exhibits the phase constitution of the bulk sample, which was consolidated from the milled powder by SPS. It is shown that the prepared bulk material contains the dominant $Mn_2N_{0.86}$ phase and a little MnO, as similar as the phase constitution demonstrated by curve "a", but with the broadened peaks due to the fine grain structure formed in the $Mn_2N_{0.86}$ bulk. From the XRD pattern, it is analyzed that the prepared $Mn_2N_{0.86}$ compound has a hexagonal structure with the lattice parameters as a = 4.818 Å and c = 4.526 Å.

From the measurement with the Archimedes method, the SPSed $Mn_2N_{0.86}$ bulk has nearly a full relative density. The microstructure of the prepared $Mn_2N_{0.86}$ bulk is shown in Fig. 2. It was observed that the ultrafine grains have the equiaxed shape, and the mean grain size was measured as approximately 150 nm. The selected area electron diffraction pattern (SAEDP) and its indexing (see the inset in Fig. 2) indicate that the $Mn_2N_{0.86}$ grains have the hexagonal crystal structure, which is consistent with the XRD analyses (referring to Fig. 1).

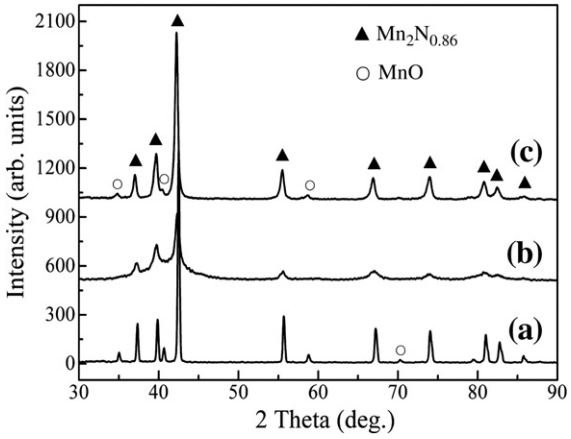


**Fig. 1.** XRD patterns of the $Mn_2N_{0.86}$ compound at different preparation stages: (a) the powder synthesized by solid-gas reaction at 1025 K for 5 h, (b) the synthesized powder after ball milling for 20 h, and (c) the ultrafine-grained bulk SPSed at 973 K for 5 min.

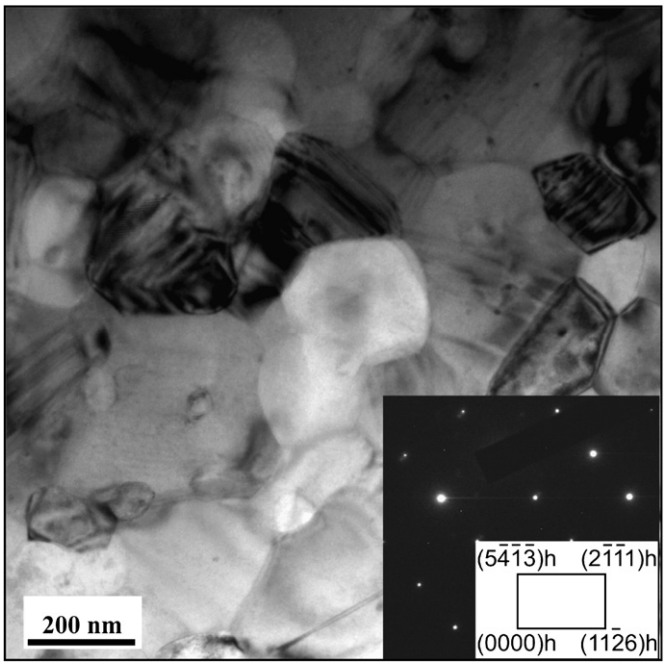


**Fig. 2.** TEM image of the microstructure of the prepared ultrafine $Mn_2N_{0.86}$ bulk. Inset: the selected area electron diffraction pattern (SAEDP) and the indexing.

Fig. 3 shows the temperature dependence of magnetization of the ball-milled powder and the ultrafine-grained bulk of $Mn_2N_{0.86}$

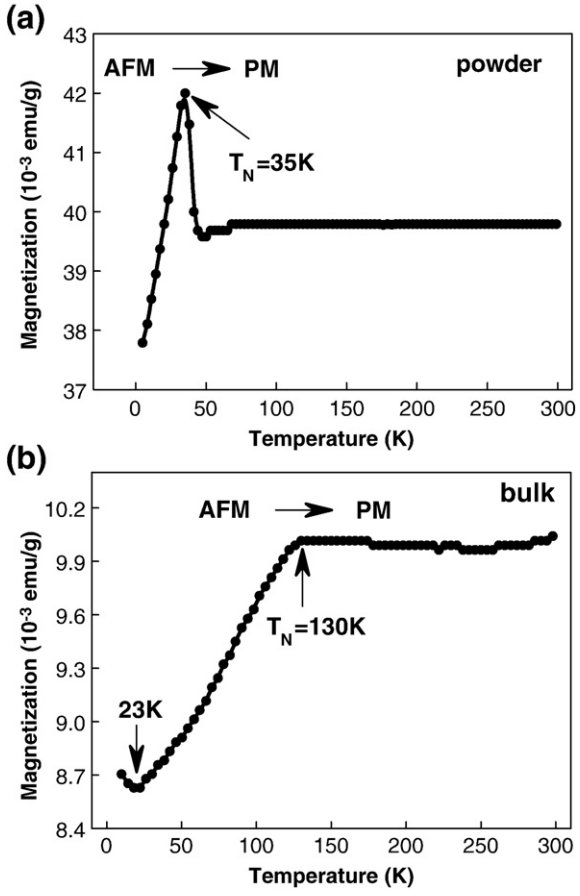


**Fig. 3.** Temperature dependence of magnetization at an external field of 500Oe: (a) the ball-milled powder, (b) the ultrafine-grained $Mn_2N_{0.86}$ compound bulk.