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Short communication

Effects of sintering temperature on microstructure, nitrogen deficiency and densification of spark plasma sintered $Mn_3Cu_{0.5}Ge_{0.5}N$

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Abstract

Single-phase $Mn_3Cu_{0.5}Ge_{0.5}N$ bulks were prepared by spark plasma sintering (SPS) in nitrogen atmosphere at different sintering temperatures, and the effects of sintering temperature on microstructure, nitrogen deficiency and densification were studied. It was found that the densification is accompanied by the thermal decomposition of $Mn_3Cu_{0.5}Ge_{0.5}N$. Nitrogen deficiency and porosity due to the thermal decomposition of the compound do not increase with increase of the sintering temperature; the nitrogen deficiency from decomposition is compensated by the diffusion of nitrogen atoms from the N_2 atmosphere. When the two processes reach the balance, minimum nitrogen deficiency of $Mn_3Cu_{0.5}Ge_{0.5}N$ is achieved together with the highest densification.

Keywords: A. Sintering; B. Microstructure; D. Nitrides; Nitrogen deficiency

1. Introduction

The excellent negative thermal expansion (NTE) properties discovered in the doped antiperovskite manganese nitrides Mn_3XN (X denotes transitional metals and/or semiconductor elements) have attracted increasing interests [1–8]. This compound is considered to be potential candidate for thermal expansion compensators, which can be widely applied in the fields of high-precision optical mirrors, dental materials, printed circuit boards, heat sinks, fuel cells, and aerospace apparatus, and etc. [9,10]. Among the single-element-doped manganese nitrides $Mn_3A_{1-x}B_xN$ (A = Cu, Zn, etc.; B = Ge, Sn, etc.), the $Mn_3Cu_{1-x}Ge_xN$ compounds showed excellent room-temperature NTE properties at a certain Ge amount, e.g. the $Mn_3Cu_{0.5}Ge_{0.5}N$ compound was found to have a linear coefficient of NTE as $-12 \times 10^{-6}\,K^{-1}$ in the temperature range 280–365 K ($\Delta T = 85$ K) [1]. However, based on the $Mn_3Cu_{1-x}Ge_xN$ compounds, the double-element-doped $Mn_3Cu_{0.6}Ge_{0.4-x}C_xN$ (C = Nb or Si) compounds exhibited the low-temperature NTE properties [5,6]. It seems that the improvement of the NTE properties of the doped manganese nitrides is limited due to the limitation of the types and contents of the doping elements. Very recently, the zero thermal expansion (ZTE) performance was found in the $Mn_3Cu_{0.5}Sn_{0.5}N_{1-\delta}$ compounds by tailoring the amount of the nitrogen deficiency (δ) [11]. The nitrogen tunable ZTE performance of the antiperovskite manganese nitrides has shown to be very important for applications.

As reported in the literature, antiperovskite manganese nitrides were fabricated by pressure-less sintering using Mn_2N powder as the starting material. Generally, the Mn_2N compound is synthesized by solid–gas reaction between Mn powder and N_2 at 700–750 °C for 60 h [6,12] and pressure-less sintering performed at 800–900 °C for 48–80 h [1,3,5]. Thus, the whole preparation route is fairly time-consuming. In our recent work [13], we proposed a rapid route to synthesize single-phase $Mn_2N_{0.86}$ by solid–gas reaction at 750 °C for 5 h. Since the $Mn_2N_{0.86}$ compound has the same crystal structure and similar magnetic features of Mn_2N, it is reasonable to substitute $Mn_2N_{0.86}$ for Mn_2N as the starting material to prepare the antiperovskite manganese nitrides. Furthermore, taking advantage of the spark plasma sintering (SPS) technique, which has been recognized as a unique rapid powder metallurgical technology applicable to various

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materials [14,15], we were able to obtain $Mn_3Cu_{0.5}Ge_{0.5}N$ bulk materials in only 10 min [8]. However, the influence of the SPS parameters on preparing the $Mn_3Cu_{1-x}Ge_xN$ bulks with a good combination of microstructure, nitrogen deficiency and density were not defined. In the present work, we develop a method to prepare $Mn_3Cu_{0.5}Ge_{0.5}N$ bulk material by performing SPS in highly purified N_2 atmosphere. Our efforts were focused on studying the effects of the sintering temperature on the microstructure, nitrogen deficiency, and densification degree of the $Mn_3Cu_{0.5}Ge_{0.5}N$ compound bulk.

2. Experimental procedure

The $Mn_2N_{0.86}$ powder was synthesized by solid–gas reaction of Mn powder (99.95% purity) and N_2 gas (99.999% purity) in a tubular furnace at 750 °C for 5 h. Then Cu (99.5% purity) and Ge (99.999% purity) powders were added into the $Mn_2N_{0.86}$ powder according to the stoichiometric ratio of the $Mn_3Cu_{0.5}Ge_{0.5}N$ compound. The three powders were mixed homogeneously, sintered by SPS (SPS 3.20-MK-V) in N_2 atmosphere at 60 MPa, heating rate of 70 °C/min and holding time of 10 min at the sintering temperature of 720 °C, 750 °C, 790 °C, 820 °C, 860 °C and 900 °C, respectively.

Phase analyses were performed by X-ray diffraction (XRD, D/max-3c, Rigaku). The microstructures were observed by Field-Emission Scanning Electron Microscope (FESEM, Nova NanoSEM-200, FEI). The nitrogen deficiency was characterized by an oxygen–nitrogen analyser (ON-3000, NCS). Density was measured by the Archimedes method. The thermal decomposition behavior of the $Mn_3Cu_{0.5}Ge_{0.5}N$ bulk was detected by thermogravimetric analyser (TG, NETZSCH STA 449C).

3. Results and discussion

3.1. Phase analysis

The XRD analyses on the phase constitution of the SPSed $Mn_3Cu_{0.5}Ge_{0.5}N$ bulk samples prepared at different sintering temperatures show $Mn_3Cu_{0.5}Ge_{0.5}N$ as the dominant phase and minor MnO (Fig. 1). The XRD data indicate that $Mn_3Cu_{0.5}Ge_{0.5}N$ has the Mn_3CuN-type antiperovskite structure (space group P*m3m*).

Single-phase $Mn_3Cu_{0.5}Ge_{0.5}N$ bulk was obtained by the SPS technique within a very short time and at relatively lower sintering temperatures. The rapid densification should be attributed to the special mechanisms related to SPS [16,17].

3.2. Microstructure

The fracture morphologies of SPSed $Mn_3Cu_{0.5}Ge_{0.5}N$ samples are shown in Fig. 2. The samples exhibit a coarse-grained structure, and a certain amount of pores in the matrix. As from the TG analysis (not shown here), the thermal

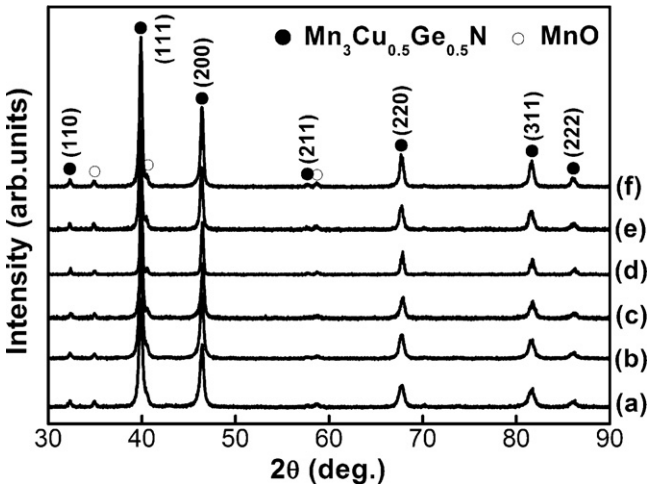

Fig. 1. XRD patterns of the prepared $Mn_3Cu_{0.5}Ge_{0.5}N$ samples SPSed at different temperatures: (a) 720 °C, (b) 750 °C, (c) 790 °C, (d) 820 °C, (e) 860 °C, (f) 900 °C.

decomposition temperature of $Mn_3Cu_{0.5}Ge_{0.5}N$ is about 690 °C. Being the sintering temperatures higher than the decomposition temperature, the pores result from the nitrogen deficiency due to the thermal decomposition of the compound. However, the amount of pores in the sample does not increase with the increase of sintering temperature. For example, it is noted that the sample sintered at 790 °C (Fig. 2c) has relatively the least pores in the microstructure. This implies that there is a balance between the nitrogen deficiency from the thermal decomposition and the nitrogen compensation due to the diffusion from N_2 atmosphere.

3.3. Nitrogen deficiency

The nitrogen deficiency of $Mn_3Cu_{0.5}Ge_{0.5}N$ samples versus sintering temperature is shown in Fig. 3. The samples prepared at 790–900 °C and 720–750 °C exhibit a continuous increase in the amount of the nitrogen deficiency, whereas at 750–790 °C, a reduced nitrogen deficiency has been observed with a relative maximum in nitrogen content in the sample sintered at 790 °C (inset in Fig. 3).

In antiperovskite Mn_3AN compounds, the interstitial nitrogen atom is generally located at the body-centered site [8] and tends to escape from the Mn_6N octahedron as the sintering temperature is higher than the decomposition temperature [11]. In the temperature range of 720–750 °C, the rate that the nitrogen atoms escape from the body-centered sites of the compound is faster than the rate that the nitrogen atoms diffuse into the compound. As a result, the nitrogen deficiency increases with increasing sintering temperature. In contrast, when the diffusion rate of nitrogen atoms in the N_2 atmosphere is higher than the decomposition rate of the compound, the nitrogen deficiency is reduced, as it occurred within the temperature range of 750–790 °C. With further increasing the temperature, as shown in the range of 790–900 °C, the nitrogen atoms diffusing into the compound are insufficient to compensate the loss of nitrogen atoms due

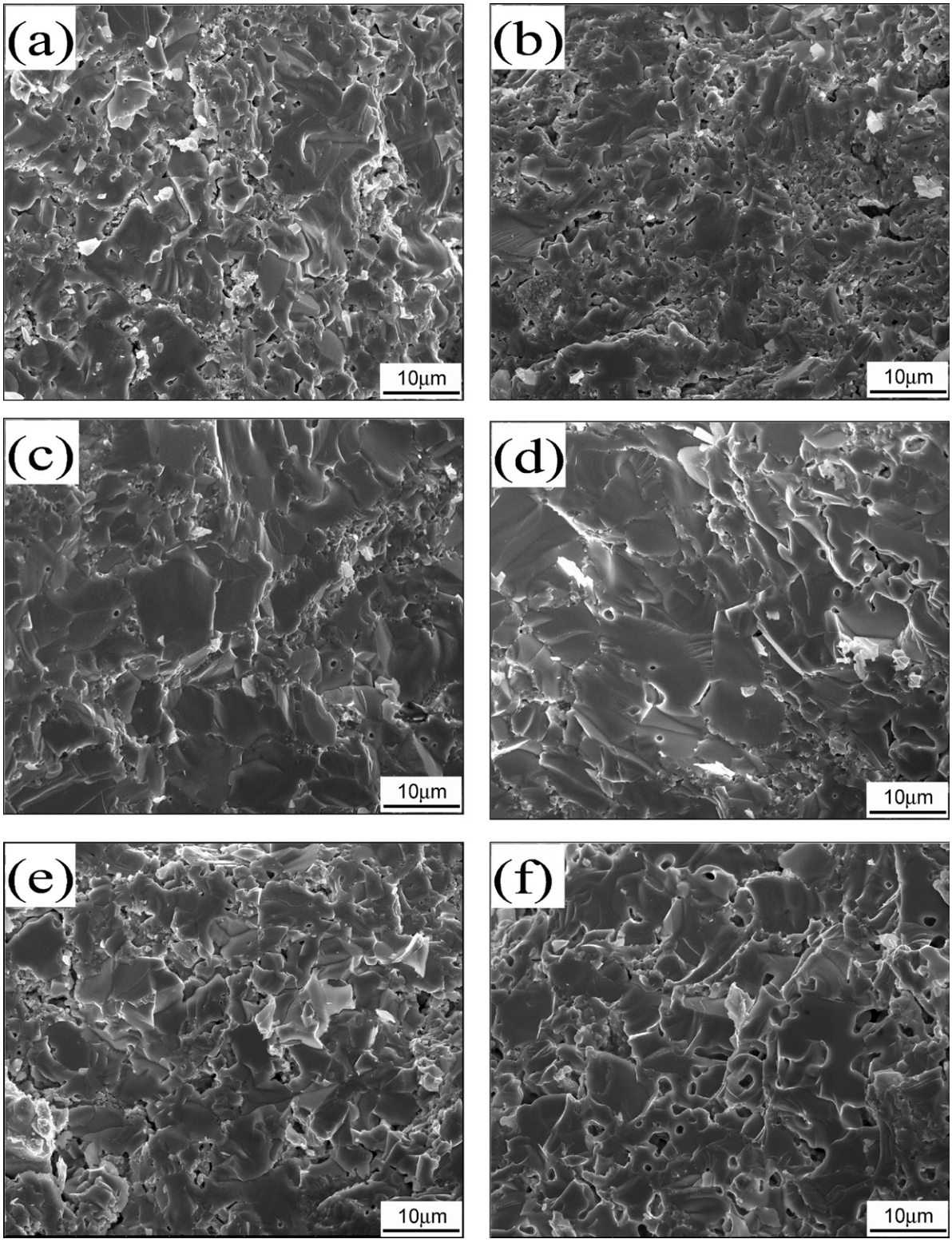

Fig. 2. SEM images of the fracture surfaces of the $Mn_3Cu_{0.5}Ge_{0.5}N$ samples SPSed at different temperatures: (a) 720 °C, (b) 750 °C, (c) 790 °C, (d) 820 °C, (e) 860 °C, (f) 900 °C.

to the drastical decomposition at high temperatures, thus the nitrogen deficiency increases again with the temperature. Therefore, when the nitrogen loss due to the decomposition is balanced with the compensation from the diffusion of nitrogen atoms, the sample has a relatively minimum nitrogen deficiency, e.g. the case at 790 °C in Fig. 3.

3.4. Densification

The relative densities of samples versus sintering temperatures are shown in Fig. 4. Due to the increasing nitrogen deficiency, the samples prepared at 720–750 °C and 790–900 °C show a decreasing relative density, while the

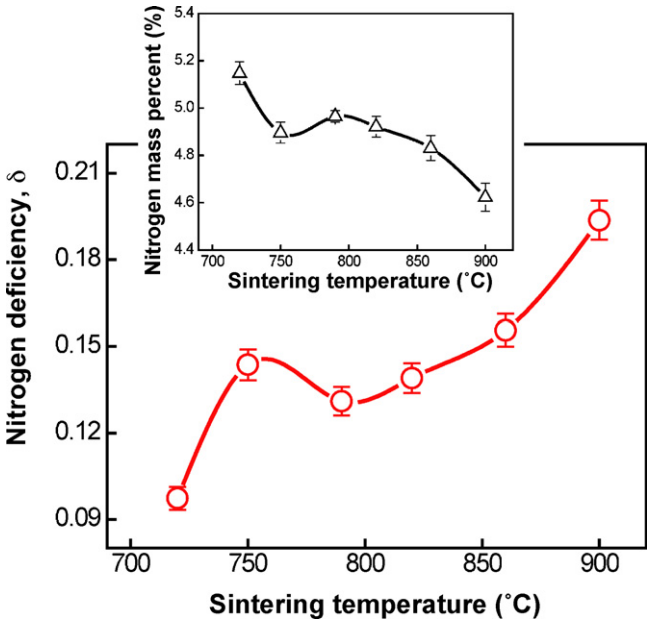

Fig. 3. Dependence of the nitrogen deficiency (δ) on the sintering temperature of the SPSed $Mn_3Cu_{0.5}Ge_{0.5}N_{1-\delta}$ samples. Inset: nitrogen mass percent via sintering temperature.

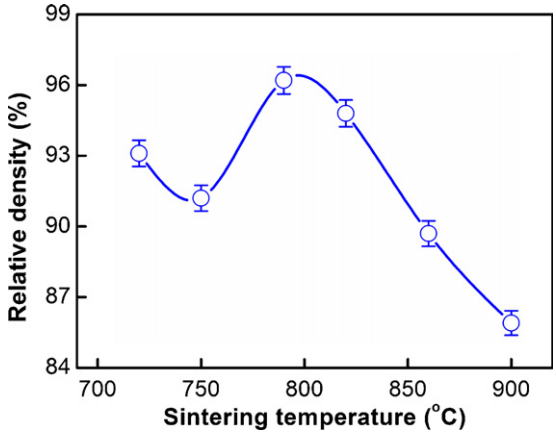

Fig. 4. Variations of the relative density of the SPSed $Mn_3Cu_{0.5}Ge_{0.5}N$ samples with the sintering temperature.

samples prepared at 750–790 °C exhibit an increasing relative density owing to the reduction of the nitrogen deficiency. Corresponding to the relatively lower nitrogen deficiency at 790 °C, the sample has the highest relative density as 96%. Although there is a very low nitrogen deficiency at 720 °C, the sample does not have the highest relative density, because the sintering temperature is not sufficient to obtain adequate densification.

4. Conclusions

Single-phase $Mn_3Cu_{0.5}Ge_{0.5}N$ bulk materials were prepared from $Mn_2N_{0.86}$ powder at 720–900 °C by SPS. It was observed that the microstructure and densification of the samples are strongly dependent on the nitrogen deficiency, which is affected by both the thermal decomposition and the diffusion of nitrogen atoms from N_2 atmosphere. The relatively lower nitrogen deficiency is obtained in the sample prepared at 790 °C, owing to the balance between the nitrogen loss due to the decomposition and the compensation from the diffusion of nitrogen atoms. Correspondingly, the sample shows the highest relative density.

Acknowledgments

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