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Effect of Microstructure Scale on Negative Thermal Expansion of Antiperovskite Manganese Nitride

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The negative thermal expansion (NTE) properties of the antiperovskite manganese nitrides with micron-scale, submicron-scale and nanometer-scale microstructures, respectively, were investigated using the $Mn_3Cu_{0.5}Ge_{0.5}N$ composition as an example. It was discovered that the NTE start temperature, NTE operation temperature range and coefficient of NTE change obviously in a wide range with decreasing the grain size level of the microstructure. The mechanisms for the broadening of the NTE operation temperature range and the decrease in the absolute value of NTE coefficient were proposed based on the grain-size-dependence of the frustrated magnetic interactions and magnetic ordering. The present study indicates that the NTE properties of the antiperovskite manganese nitrides can be tailored by the control of the microstructure scale.

KEY WORDS: Negative thermal expansion; Antiperovskite manganese nitride; Magnetic interaction; Microstructure scale

1. Introduction

Materials having the negative thermal expansion (NTE) properties are significant for both scientific research and technological applications[1−4]. The NTE materials are generally used to fabricate the zero thermal expansion (ZTE) composites by being combined with the usual positive thermal expansion (PTE) materials[5,6]. Recently, the antiperovskite manganese nitrides in a form of Mn_3AN (A=Cu, Zn, Ga, etc.) have attracted increasing attentions due to the findings of their excellent NTE properties[7−13]. Moreover, as compared with other types of NTE materials, the Mn_3AN compounds have shown the advantages of isotropic NTE behavior, adjustable coefficient of NTE (α) and operation temperature range (ΔT), and high electrical and thermal conductivity[7,9,14].

As reported in literature[7,13], in the class of Mn_3AN-type NTE materials the Ge-doped Mn_3CuN compounds exhibited outstanding NTE properties. It was found that in the $Mn_3Cu_{1-x}Ge_xN$ compounds the large magnetovolume effect (MVE) could be obtained by substituting Ge for a certain amount of Cu[7], by which the NTE properties were improved. In particular, among various compositions the $Mn_3Cu_{0.5}Ge_{0.5}N$ compound was found to have the largest operation temperature range as $\Delta T = 85$ K, with the coefficient of NTE as $\alpha = -12 \times 10^{-6}$ K^{-1}[7]. For the $Mn_3Cu_{1-x}Ge_xN$ compounds, the large MVE and the continuous NTE behavior over a relatively wide temperature range were attributed to the geometrical frustration of the Mn magnetic moments[15]. However, the in-depth studies on the factors that influence the frustrated interactions of the magnetic moments and hence affect the MVE and the NTE properties have been rarely reported so far.

In the present paper, our studies are focused on the dependence of the NTE properties of the antiperovskite manganese nitride on the microstructure scale. In the experiments, compound bulks with a same composition of $Mn_3Cu_{0.5}Ge_{0.5}N$ but different microstructure scales, i.e. the micron-, submicron- and nanometer-scale grain structures, respectively, were prepared by the newly developed routes. The NTE properties were characterized, and the mechanisms for the grain size effects on the NTE properties of the antiperovskite manganese nitrides were proposed based on the studies on the grain-size-dependence of the frustrated magnetic interactions and the magnetic ordering.

2. Experimental

2.1. Preparation of $Mn_3Cu_{0.5}Ge_{0.5}N$ compound bulks with different microstructure scales

The $Mn_3Cu_{0.5}Ge_{0.5}N$ compound bulk with the micron-scale microstructure was prepared by spark plasma sintering (SPS) the mixture of Cu, Ge and $Mn_2N_{0.86}$ powders[16], designed

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according to the stoichiometric composition. The powder mixture was fed into a graphite die and then sent to the sintering chamber of the SPS equipment, which was installed in a completely closed system[17,18]. The powder mixture was sintered at 820 °C for 10 min under a constant pressure of 60 MPa.

The $Mn_3Cu_{0.5}Ge_{0.5}N$ compound bulk with the submicron-scale microstructure was fabricated by a route of concurrent crystallization and densification of an amorphous powder. Firstly, the amorphous $Mn_2N_{0.86}$ powder was prepared by milling the single-phase $Mn_2N_{0.86}$ powder with a ball-to-powder weight ratio (BPR) of 30:1 for 40 h. Then the amorphous $Mn_3Cu_{0.5}Ge_{0.5}N$ powder was obtained by milling the mixture of Cu, Ge and amorphous $Mn_2N_{0.86}$ powders with a BPR of 10:1 for 20 h. Finally, the ultrafine-grained $Mn_3Cu_{0.5}Ge_{0.5}N$ compound bulk was prepared by spark plasma sintering the amorphous powder using the same sintering parameters as those for the compound bulk with the micron-scale microstructure.

For the preparation of the $Mn_3Cu_{0.5}Ge_{0.5}N$ compound bulk with the nanometer-scale microstructure, firstly the amorphous powder was obtained by directly milling the previously prepared $Mn_3Cu_{0.5}Ge_{0.5}N$ compound with the micron-scale microstructure, with a BPR of 30:1 for 30 h. Subsequently, the amorphous powder was put into a die made of tungsten carbides and then sent to the SPS equipment. The powder was sintered at 550 °C for 3 min under a constant pressure of 400 MPa.

In the above routes, the ball-milling and SPS procedures were carried out in the argon and nitrogen atmosphere, respectively, to prevent the samples from contamination. Moreover, the use of the nitrogen atmosphere in the SPS process was also for a purpose of compensating the nitrogen loss at high sintering temperatures.

2.2. Characterization of structures and properties

The phase constitutions of the prepared $Mn_3Cu_{0.5}Ge_{0.5}N$ compound bulks were detected by X-ray diffraction (XRD, D/max-3c, Rigaku) with Cu$K\alpha$ radiation. The microstructures of the different compound bulks were observed using the transmission electron microscopy (TEM, JEOL 3010 and JEOL JEM 2100F) operated at 200 kV. The grain sizes in the micron- and submicron-scale microstructures were measured by the linear intercept method applied to the microscopy images. The grain sizes in the nanometer-scale microstructure were measured in TEM with a recently developed method to separate overlapping grains and to determine the size distribution with sufficient statistics[19,20]. The NTE properties of the compound bulks were characterized by the temperature-varying XRD analyzer (X'Pert Pro MPD, Philips) in a temperature range from 77 K to 400 K. The zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves of the compound bulks were measured using a superconducting quantum interference device (SQUID) magnetometer in a temperature range from 5 K to 400 K with a magnetic field of 500 Oe.

3. Measurement Results

3.1. Phase constitution

The XRD patterns of the $Mn_3Cu_{0.5}Ge_{0.5}N$ compound bulks with different microstructure scales are shown in Fig. 1. As indicated by the indexing, all the samples have the antiperovskite Mn_3CuN-type crystal structure (space group Pm-3m). A little amount of MnO exists in the compounds, which is considered to be introduced in the preparation procedures[16]. As shown in Fig. 1(d), in a unit cell of the $Mn_3Cu_{0.5}Ge_{0.5}N$ crystal structure, the Cu/Ge atoms share the corner sites in the cubic lattice, and the Mn and N atoms locate at the face-centered and body-centered sites, respectively.

3.2. Microstructures

Fig. 2 shows the microstructures with different scales of the $Mn_3Cu_{0.5}Ge_{0.5}N$ compound bulks and the corresponding grain size distributions. The micron-scale microstructure (Fig. 2(a)) has a grain size distribution in a range of 1.0−5.0 μm with an average grain size of 2.2 μm (Fig. 2(b)). The submicron-scale microstructure (Fig. 2(c)) has a grain size distribution of 120−730 nm and an average grain size of 350 nm (Fig. 2(d)). The nanometer-scale microstructure (Fig. 2(e)) contains nanoscale grains in a range of 12−33 nm with an average grain size of 20 nm (Fig. 2(f)). The selected area electron diffraction (SAED) patterns of the samples indicate that the compounds have the antiperovskite Mn_3CuN-type crystal structure, which is consistent with the XRD analysis (Fig. 1).

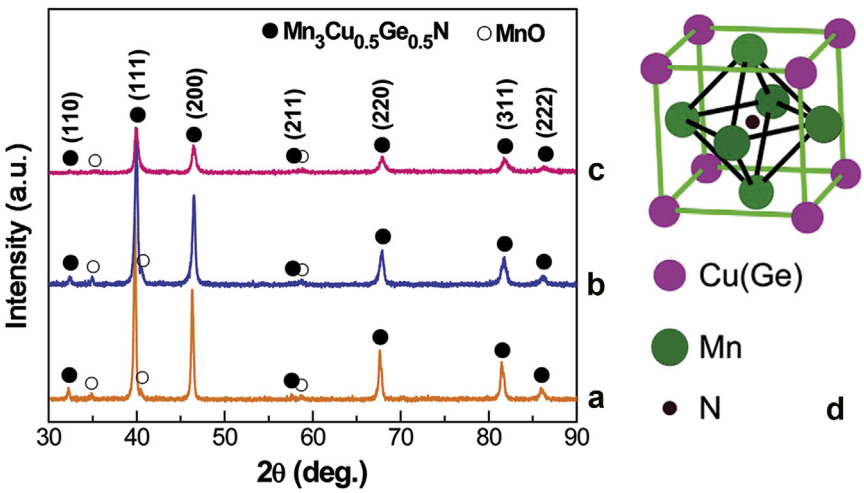

Fig. 1 XRD patterns of the $Mn_3Cu_{0.5}Ge_{0.5}N$ compound bulks with micron-scale (a), submicron-scale (b) and nanometer-scale microstructures (c), and the diagram for the crystal structure (d).