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Negative thermal expansion and electrical properties of $Mn_3(Cu_{0.6}Nb_xGe_{0.4-x})N$ (x=0.05–0.25) compounds

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Abstract

Bulk materials with the general formula of $Mn_3(Cu_{0.6}Nb_xGe_{0.4-x})N$ (x=0.05, 0.1, 0.15, 0.2, 0.25), $Mn_3(Cu_{0.6}Ge_{0.4})N$ and $Mn_3(Cu_{0.7}Ge_{0.3})N$ were fabricated by mechanical ball milling and solid state sintering. Their thermal expansion coefficients and electrical conductivities were investigated in the temperature range of 80–300 K. It is found that the temperature interval of negative temperature expansion behavior is about 95 K in the samples of $Mn_3(Cu_{0.6}Nb_{0.15}Ge_{0.25})N$ and $Mn_3(Cu_{0.6}Nb_{0.2}Ge_{0.2})N$, which is twice as large as that of $Mn_3(Cu_{0.7}Ge_{0.3})N$. The negative thermal expansion of $Mn_3(Cu_{0.6}Nb_{0.15}Ge_{0.25})N$ can reach to -19.5×10^{-6} K^{-1} in the temperature range of 165 to 210 K. The electrical conductivity of this series materials is in a level of about 2.5×10^6 $(\Omega\ m)^{-1}$.

Keywords: Thermal properties; Electrical Properties; Cryogenic temperature

1. Introduction

It is well known that the majority of materials usually show a positive thermal expansion with increasing temperature. Thermal expansion is a critical parameter that must be considered in the design of precision devices [1]. Thermal expansion mismatch between component materials can cause stresses and deformations that will lead to reliability problems. In cryogenic engineering, materials will undergo thermal shock when temperature varies between room temperature and cryogenic temperature. The performance of precision devices has been limited by the problem induced by the thermal expansion between different materials. For example, the refrigeration efficiency of piston refrigerator will be decreased when piston to cylinder wall clearance change introduced by the difference thermal expansion coefficient of piston and cylinder. To avoid this problem, one of the possible methods is to develop a controllable expansion coefficient material obtained by compounding isotropic negative thermal expansion material with other positive expansion material. Negative thermal expansion materials contract when heated and expand on cooling [2–4]. Negative thermal expansion materials are known in several oxide systems. Such as, ZrW_2O_8 [5,6], HfW_2O_8 [7], they have large negative thermal expansion coefficients in a wide temperature interval, but their mechanical and electrical properties are poor.

Ge-doped manganese nitride negative thermal expansion material discovered by Koshi Takenaka and Hidenori Takagi [1,8] is a new material, which with the large negative thermal expansion coefficient and good mechanical property, electrical conductivity and thermal conductivity. This series material shows excellent negative thermal expansion property around and above room temperature, Such as $Mn_3(Cu_{0.53}Ge_{0.47})N$, $Mn_3(Cu_{0.5}Ge_{0.5})N$, which show NTE of $\alpha=-16\times10^{-6}$ K^{-1} at T=267–342 (ΔT=75 K) and $\alpha=-12\times10^{-6}$ K^{-1} at T=280–365 (ΔT=85 K), respectively [8]. However, the temperature interval of negative thermal expansion (NTE) behavior of this series material occurs at cryogenic temperature is very narrow, which makes it of little practical use in cryogenic engineering.

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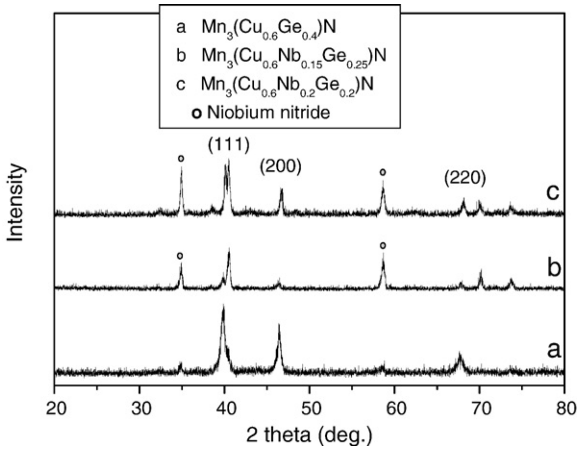

Fig. 1. XRD patterns of $Mn_3(Cu_{0.6}Ge_{0.4})N$, $Mn_3(Cu_{0.6}Nb_{0.15}Ge_{0.25})N$ and $Mn_3(Cu_{0.6}Nb_{0.2}Ge_{0.2})N$.

In order to promote the practical applications, the potential payoff for the development of this series material with wide temperature interval of NTE behavior at cryogenic temperature is of great interest, and further investigation of their physical properties is also required.

In the present study, bulk materials with the general formula of $Mn_3(Cu_{0.6}Nb_xGe_{0.4-x})N$ (x=0.05, 0.1, 0.15, 0.2, 0.25), $Mn_3(Cu_{0.6}Ge_{0.4})N$ and $Mn_3(Cu_{0.7}Ge_{0.3})N$ were fabricated by mechanical ball milling and solid state sintering processing. Structural study was performed using X-ray diffraction. Their thermal expansion coefficient and electrical conductivity were investigated in the temperature range of 80–300 K.

2. Experimental procedure

Polycrystalline samples were prepared through a solid state reaction. Pure metal powders of Cu (99.99%), Nb (99.99%), Ge (99.999%) and Mn (99.99%) with initial particle size of about 50 μm were used as starting materials. Firstly, Mn_2N powders were synthesized by flowing purified nitrogen gas into Mn powders at 750 °C for 60 h, then put Cu, Nb, Ge and Mn_2N powders together into the agate jars with agate balls under purified argon atmosphere. The ball-to-powder weight ratio was 20:1. Mechanical ball milling was conducted in a planetary ball milling at the rotating speed of 400 rpm for 24 h. The as-milled powders were preformed under a pressure of 500 MPa by cold press, then wrapped with tantalum foil and sintered at 800 °C under purified argon atmosphere for 48 h [9,10]. X-ray diffraction patterns of the resulting pellet were investigated by X-ray diffraction (XRD) at room temperature with a Rigaku D/max-RB diffractometer using Cu radiation (λ=0.154056 nm). Linear thermal expansion $\Delta L/L_{(295\ K)}$ was measured using strain gage [8]. This method requires a material of known expansion. We used fused silica and the corresponding thermal expansion data [11]. Electrical conductivity was measured in the temperature range of 80–300 K by standard four-probe method. The densities of the sintered samples are measured by using the Archimedes method.

Table 1
The temperature interval of NTE behavior and thermal expansion coefficients in the temperature ranges of NTE behavior

Samples	T_{start} (K)	T_{end} (K)	ΔT (K)	Thermal expansion coefficient (10^{-6} K^{-1})
$Mn_3(Cu_{0.6}Ge_{0.4})N$	295	237	58	−17.17
$Mn_3(Cu_{0.6}Nb_{0.05}Ge_{0.35})N$	281	219	62	−5.08
$Mn_3(Cu_{0.6}Nb_{0.1}Ge_{0.3})N$	256	199	57	−19.93
$Mn_3(Cu_{0.6}Nb_{0.15}Ge_{0.25})N$	221	128	93	−11.30
$Mn_3(Cu_{0.6}Nb_{0.2}Ge_{0.2})N$	172	77	95	−5.71

3. Results and discussion

3.1. Structures

Fig. 1 gives the X-ray diffraction patterns of the $Mn_3(Cu_{0.6}Ge_{0.4})N$, $Mn_3(Cu_{0.6}Nb_{0.15}Ge_{0.25})N$ and $Mn_3(Cu_{0.6}Nb_{0.2}Ge_{0.2})N$ samples. The

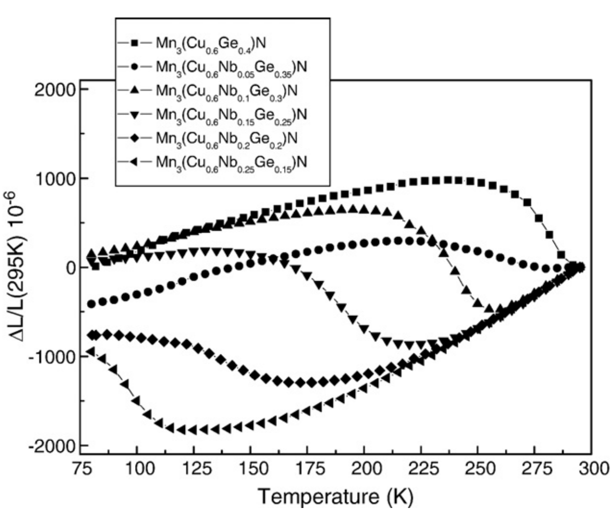

Fig. 2. Linear thermal expansion of the samples.

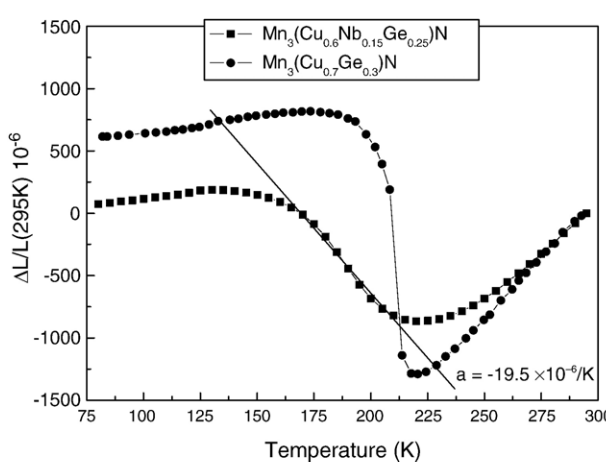

Fig. 3. Linear thermal expansion of $Mn_3(Cu_{0.6}Nb_{0.15}Ge_{0.25})N$ and $Mn_3(Cu_{0.7}Ge_{0.3})N$.

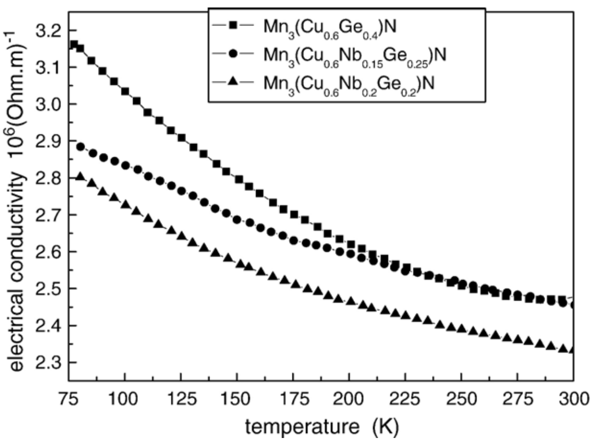

Fig. 4. Electrical conductivity versus temperature for samples $Mn_3(Cu_{0.6}Ge_{0.4})N$, $Mn_3(Cu_{0.6}Nb_{0.15}Ge_{0.25})N$ and $Mn_3(Cu_{0.6}Nb_{0.2}Ge_{0.2})N$.

XRD patterns show that these samples have a dominating phase with the Mn_3CuN-type structure (space group, Pm3m) (JCPDS Card, No. 23-0220). However, other diffraction peaks are found in the samples doped with Nb. The relative intensities of diffraction peaks, corresponding to 2θ-angle of about 35° and 60°, increased with increasing Nb. These diffraction peaks derived from the niobium nitride (JCPDS Card, No. 65-5011). It can therefore be estimated that much more existence of niobium nitride might influence the negative thermal expansion property and other physical properties. The density of the sintered samples is about 6.1 g/cm^3.

3.2. Negative thermal expansion property

Fig. 2 displays linear thermal expansion $\Delta L/L_{(295\ \mathrm{K})}$ data versus temperature for samples $Mn_3(Cu_{0.6}Nb_xGe_{0.4-x})N$ (x=0, 0.05, 0.1, 0.15, 0.2, 0.25). It is clear that the linear thermal expansion $\Delta L/L_{(295\ \mathrm{K})}$ data of all samples increased with decreasing temperature within a certain temperature ranges. It means that all samples show NTE behavior in these temperature ranges. The sample $Mn_3(Cu_{0.6}Ge_{0.4})N$ displays negative thermal expansion behavior in the temperature range of 295–237 K. The temperature ranges of negative thermal expansion behavior of $Mn_3(Cu_{0.6}Nb_xGe_{0.4-x})N$ (x=0.05, 0.1, 0.15, 0.2) are summarized in Table 1. From these data, we find that the temperature range of NTE behavior shifts toward low temperature region. It suggests that the temperature range of NTE behavior is affected by the partial replacement of Ge by Nb.

From Fig. 2, we can also find that the temperature interval of NTE behavior (ΔT) broadens with increasing of the Nb content. It is important to note that the ΔT of the samples $Mn_3(Cu_{0.6}Nb_{0.15}Ge_{0.25})N$ and $Mn_3(Cu_{0.6}Nb_{0.2}Ge_{0.2})N$ are 93 K and 95 K, respectively, which are about 60% larger than that of $Mn_3(Cu_{0.6}Ge_{0.4})N$. For comparison, the linear thermal expansion $\Delta L/L_{(295\ \mathrm{K})}$ data as a function of temperature for samples $Mn_3(Cu_{0.6}Nb_{0.15}Ge_{0.25})N$ and $Mn_3(Cu_{0.7}Ge_{0.3})N$ are shown in Fig. 3. It is of particular interest that the ΔT of the sample $Mn_3(Cu_{0.6}Nb_{0.15}Ge_{0.25})N$ is twice as large as that of sample $Mn_3(Cu_{0.7}Ge_{0.3})N$. If the thermal expansion coefficient of $Mn_3(Cu_{0.6}Nb_{0.15}Ge_{0.25})N$ is considered from 221 to 128 K, we will have the average thermal expansion coefficient $-11.3\times10^{-6}\ \mathrm{K}^{-1}$. And the linear thermal expansion $\Delta L/L_{(295\ \mathrm{K})}$ data is linear with the temperature in the temperature rang of 210 to 165 K, in which thermal expansion coefficient is $-19.5\times10^{-6}\ \mathrm{K}^{-1}$. The absolute magnitude of this negative thermal expansion coefficient is larger than its positive counterpart seen in typical metals, such as copper ($16.7\times10^{-6}\ \mathrm{K}^{-1}$ at 300 K and $15.57\times10^{-6}\ \mathrm{K}^{-1}$ at 210 K [12]).

It is also noted that the values of linear thermal expansion $\Delta L/L_{(295\ \mathrm{K})}$ data of samples $Mn_3(Cu_{0.6}Nb_{0.15}Ge_{0.25})N$, $Mn_3(Cu_{0.6}Nb_{0.1}Ge_{0.3})N$ and $Mn_3(Cu_{0.6}Ge_{0.4})N$ are very small at liquid nitrogen temperature. It means that the volumes of these materials at liquid nitrogen temperature are equal with that at room temperature. It is also of particular interest that the variation of the linear thermal expansion $\Delta L/L_{(295\ \mathrm{K})}$ data of sample $Mn_3(Cu_{0.6}Nb_{0.15}Ge_{0.25})N$ are small in the temperature range of 180–78 K. It indicates that this material shows the Invar-like behavior in this temperature range.

From the data presented above, it can be seen that the broadening ΔT material at cryogenic temperature was obtained by doping $Mn_3(Cu_{0.6}Ge_{0.4})N$ with Nb. However, it is not even clear why the addition of Nb can broaden ΔT. In Koshi Takenaka and Hidenori Takagi's previous study on the $Mn_3(Cu_{1-x}Ge_x)N$, they suspect that Ge may give rise to a strong local disorder, which might give rise to a relaxor-like behavior as in relaxor ferroelectrics or relaxor ferromagnets [8]. In our study, we found niobium nitride in the samples of $Mn_3(Cu_{0.6}Nb_{0.15}Ge_{0.25})N$ and $Mn_3(Cu_{0.6}Nb_{0.2}Ge_{0.2})N$ (see Fig. 1). The existence of niobium nitride might strengthen the local disorder, and further broaden ΔT. The microscopic origin of this phenomenon will be further investigated in future work.

3.3. Electrical conductivity

Electrical conductivity is an important parameter for material. For many applications, electrical conductivity of negative thermal expansion material must be considered. The electrical conductivity versus temperature for samples $Mn_3(Cu_{0.6}Ge_{0.4})N$, $Mn_3(Cu_{0.6}Nb_{0.15}Ge_{0.25})N$ and $Mn_3(Cu_{0.6}Nb_{0.2}Ge_{0.2})N$ are shown in Fig. 4. The electrical conductivities of these series materials are in a level of about $2.5\times10^6\ (\Omega\ \mathrm{m})^{-1}$. It is clear that electrical conductivities decrease monotonously with increasing temperature in the whole measuring range, being characteristic of metal. Electrical conductivities decreased with increasing Nb.

4. Conclusions

We have successfully obtained the Nb and Ge-doped manganese nitrides negative thermal expansion materials by the mechanical ball milling and solid state sintering. The temperature interval of negative thermal expansion behavior of about 95 K was obtained in the sample of $Mn_3(Cu_{0.6}Nb_{0.15}Ge_{0.25})N$, $Mn_3(Cu_{0.6}Nb_{0.2}Ge_{0.2})N$ at cryogenic temperature. The $Mn_3(Cu_{0.6}Nb_{0.15}Ge_{0.25})N$ shows negative thermal expansion of$-19.5\times10^{-6}\ \mathrm{K}^{-1}$ in the temperature range of 165 to 210 K. The electrical conductivities of this series material are in a level of about $2.5\times10^6\ (\Omega\ \mathrm{m})^{-1}$. This series isotropic and large negative thermal expansion material is desirable for cryogenic application.

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