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Negative Thermal Expansion in $Mn_3Ga(Ge,Si)N$ Anti-perovskite Materials

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Abstract. Mn_3GaN has anti-perovskite structure and there exists an abnormal thermal expansion behavior in accompanying with a magnetic transition and variation of electronic transport properties. Substitution of Ga by Ge(Si) induces the change of the thermal expansion properties and the corresponding temperature range. The structure, heat capacity, magnetic and electronic transport properties of $Mn_3Ga(Ge,Si)N$ were investigated and discussed.

Introduction

Anti-perovskite manganese compounds Mn_3XN (X=Ga, Al, Zn, Cu and Sn) are well known for a couple of years[1-2,4-9]. In Mn_3XN, the magnetic Mn atoms are located at the face-centered positions, and the N atom at the body-centered position. As this is opposite to the structure of perovskite, we call them anti-perovskite[3]. The crystal structure is shown in Fig.1. In spite of the simple crystal structure, these compounds show a wide variety of novel physical phenomena such as superconductivity, giant magnetoresistivity and a nearly zero temperature coefficient of resistivity[10-14]. Therefore, these compounds with anti-perovskite structure have attracted great attentions.

There exists a magnetic phase transition in Mn_3XN compounds at certain temperature, accompanied by a large discontinuous contraction of the lattice with increasing temperature. Due to the sharp change of the lattice volume, it's not suitable as negative thermal expansion (NTE) materials for actual applications.

The discovery of strong NTE effects over a broad temperature range in ZrW_2O_8 has stimulated interest in the study of NTE materials. Very recently, K. Takenaka *et al.* found that the discontinuous lattice contraction in the vicinity of the magnetic transition temperature T_c was successfully modified into continuous contraction by introducing the element Ge into anti-perovskite manganese nitrides[15-16]. So the study of $Mn_3X(Ge)N$ has regained great interests because of its metallic property and controllable negative thermal expansion.

In this paper, we report the thermal expansion properties of Mn_3Ga (Ge, Si) N compounds by variable temperature X-ray diffraction measurements. The dependence of magnetization, electrical resistivity and heat capacity on temperature in the manganese-based anti-perovskite materials were measured. The close correlation among lattice, magnetic and electronic transport properties were discussed.,

Experiments

Polycrystalline samples of Mn_3GaN, $Mn_3Ga_{0.5}Ge_{0.37}Si_{0.13}N$ and $Mn_3Ga_{0.5}Si_{0.5}N$ were prepared by solid-state reaction using powders of GaN, Mn, Si_3N_4 and Ge as the starting materials. Stoichiometric amounts of the starting materials were mixed and pressed into pellets. The pellets were wrapped in a Ta foil and then vacuum sealed in a small quartz tube. The quartz tube was sintered in a box furnace at 750°C for 80 h, and then cooled down to room temperature.

X-ray diffraction patterns at room temperature were obtained from a Rigaku D/MAX 2200PC diffractometer using CuKα radiation. Fig. 2 shows the XRD pattern of the Mn_3GaN sample, which

shows a single phase with anti-perovskite structure. A software named Powder X[18] was used for indexing and lattice parameter calculation. The cubic lattice parameters were obtained with a=3.898 Å, 3.878 Å and 3.837Å for Mn_3GaN, $Mn_3Ga_{0.5}Ge_{0.37}Si_{0.13}N$ and $Mn_3Ga_{0.5}Si_{0.5}N$, respectively. From the results, we can see the distinct difference of the lattice parameter (a) for different samples, which indicates the doping effect of Ge and Si.

For the measurements of coefficient of thermal expansion (CTE), variable temperature X-ray diffraction from room temperature to 523 K was done for these samples on a X'Pert PRO MPO diffractometer. Magnetization was measured at 5000 Oe by Lake Shore 7410 VSM (room temperature $\leq T \leq 500K$). A physical property measurement system (PPMS) was employed to collect the resistivity data from 280 K to 400 K. Heat capacity analysis was conducted using TAQ200 DSC in the temperature range from 270 K to 470 K.

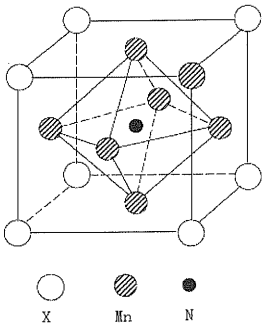

Fig.1 the crystal structure of Mn_3XN

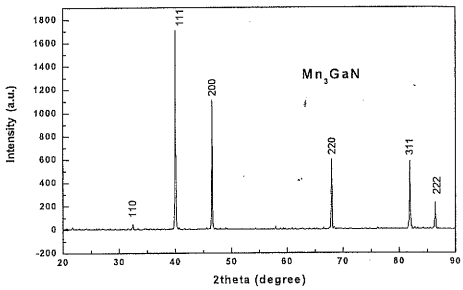

Fig.2 XRD pattern of Mn_3GaN

Results and discussion

As shown in Fig.3(a), there exists a big abrupt drop of lattice constant for Mn_3GaN starting from 348 K and finishing at 361 K, without breaking the cubic symmetry. The temperature range is Δ T=13 K, while K. Takenaka[15] only reported the change of thermal expansion behavior for the material by measuring $\Delta L/L$ using a strain gauge, which is not intrinsic. Before 348 K, the lattice constant keeps almost unchanged with increasing temperature from 290 K, which implied the occurrence of near zero thermal expansion. The transition is corresponding to a magnetic phase transition from antiferromagnetic (AFM) to paramagnetic (PM) state with increasing temperature, which can be seen in Fig.5.

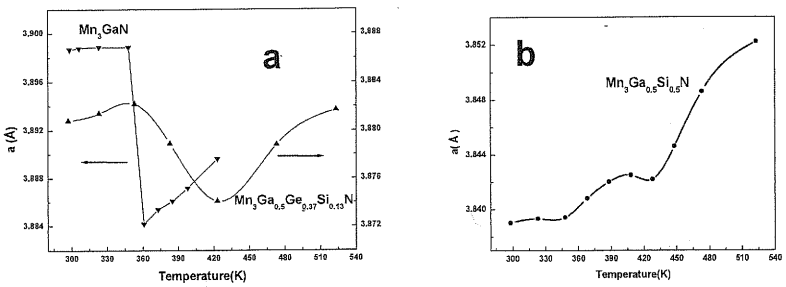

Fig.3 Temperature dependence of the lattice parameters by XRD
(a : Mn_3GaN and $Mn_3Ga_{0.5}Ge_{0.37}Si_{0.13}N$, b : $Mn_3Ga_{0.5}Si_{0.5}N$)

When both Ge and Si were introduced to replace Ga in Mn_3GaN to form $Mn_3Ga_{0.5}Ge_{0.37}Si_{0.13}N$, it was found that the thermal expansion behavior was very different. The phase transition process was retarded to higher temperature. The sharp lattice contracting process was broadened and the

temperature range increases to △ T=70 K from 353 K to 423 K, as seen in Fig. 3(a). The thermal expansion coefficient in the temperature region was determined as about $\alpha=-2.8\times10^{-5}$ /K (353 K-423 K).

It can be speculated that the volume saltation near T_N for Mn_3GaN results from the abrupt charge transfer between the spin-polarized bands due to the AFM –PM transition. So we think that the electronic band structure of Mn_3XN compounds holds the key to understand the broadening by Ge doping. Narrow bands are formed near the Fermi level by the strong hybridation between N 2p and Mn 3d orbitals. The occupation of these narrow bands is sensitively changed according to the number of the valence electron on X, while the X atoms provide the itinerant electrons at the Fermi level. Thus, the number of valence electrons on X is a dominant factor for the structural and magnetic properties. The discussion from Ref.[20] supports our point.

For further understanding the effects of Ge dopant, there are several assumptions to explain the phenomena. We think that the first-order transition may be gradually changed into the second-order with increasing Ge-dopant. Jardin et al. have performed a band calculation of cubic perovskite compounds Mn_3XN by applying a simple tight-binding approximation to the d electrons of Mn atoms and p electrons of N atoms[19]. They found a sharp singularity in the electronic density of states at the Fermi level and pointed out the Fermi energy E_F lies very close to the infinite singularities energy E_s in Mn_3XN. According as the Fermi energy E_F is smaller or larger than E_s, the structure transition is a first-order phase transition, and the latent heat is the larger as $|E_F-E_s|$ is the larger. When $E_F=E_s$, a second-order phase transition can be obtained. The parameter $|E_F-E_s|$ could depend on the exact chemical composition of a given compound, and could vary from one compound to another. In Mn_3GaN, there is a shift of the Fermi level after Ge introduced. In addition, the crystal and spin structures of Mn_3GeN are distinct from other Mn_3XN members. A tetragonal distortion in Mn_3GeN may remove the degeneracy of the narrow band p-d_{eg}[20], and the sharp singularity of the density of states E_s can be split into several new singularities by small lattice distortion. So it is possible that partial Ge-doping just has E_F lie in E_s, and the first-order transition is changed into the second-order. Another probability is that the sharp peak near the E_F may be broaden or smeared out with doping, while the DOS near E_F must be modified by Ge-doping, then as a result the transition is retarded.

To testify the above assumptions, the thermodynamic property was investigated. Fig. 4 gives the dependence of isobaric heat capacity C_p on temperature. For Mn_3GaN, upon heating, a sharp and narrow peak is detected at T=335 K for ΔT=10 K. In addition, an obvious endothermic peak is observed from the DSC curve, shown in inset of Fig.4 (a), which is indicative of the first-order phase transition.

A different shape in the C_p–T curve for $Mn_3Ga_{0.5}Ge_{0.37}Si_{0.13}N$ is shown in Fig.4 (b). An anomaly of heat capacity is observed from 327 K to 430 K with the peak at 405 K. No endothermic peak occurs

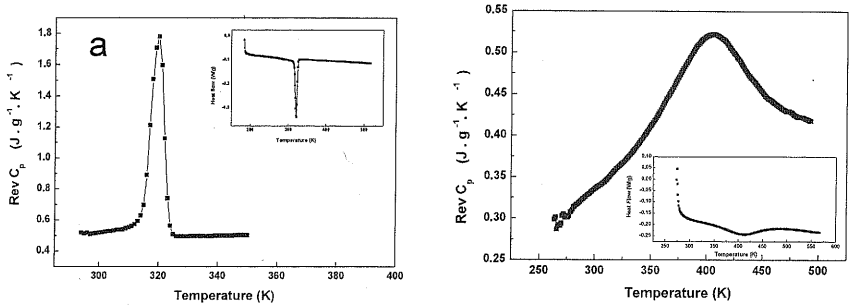

Fig. 4 Variation of the heat capacity with temperature for the sample (a) Mn_3GaN, (b) $Mn_3Ga_{0.5}Ge_{0.37}Si_{0.13}N$, Inset shows the DSC curves of the samples.

in DSC curve. The excess heat capacity above the phase transition temperature decreases with increasing temperature. Although the excess heat capacity is a little broad, the shape is similar with λ-type, which is a general characteristic of the second-order phase transition[21-22]. This characteristic indicates a qualitative change in transition behavior of the solid solution.

However, if only having Si doping, not only the broadening of the negative thermal expansion behavior did not be observed which was shown in Fig.3 (b), but also the sudden volume change in Mn_3GaN disappeared. Moreover, so far no other element was reported to have the broadening effect like Ge. The uniqueness and the true origin of Ge- doping effect needs to be confirmed by further experiments.

In addition, the variation of magnetization with temperature was measured for analysing the essence of the transition further. From Fig.5, an antiferromagnetic(AFM)- paramagnetic(PM) transition was found. The Neel transition temperature is T_N=353 K and T_N=400 K for Mn_3GaN and $Mn_3Ga_{0.5}Ge_{0.37}Si_{0.13}N$, respectively. Ge doping induces a big shift (47 K) of the Neel transition temperature to higher temperature. The critical temperature point for Mn_3GaN agrees well with the lattice saltation as shown in Fig.3 (a). The simultaneous occurrence of abnormal lattice change and magnetic transition is always observed in these magnetic materials. Although there is a small deviation for $Mn_3Ga_{0.5}Ge_{0.37}Si_{0.13}N$ while the lattice saltation starts at about T=353 K, we can speculate that the structure transition is colse related to the magnetic transion from the result.

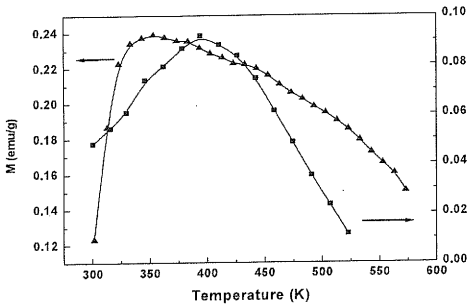

Fig.5 Temperature dependence of the magnetization of Mn_3GaN (▲ symbol) and $Mn_3Ga_{0.5}Ge_{0.37}Si_{0.13}N$ (■ symbol)

As there is a close correlation among lattice, spin, and charge in the manganese-based antiperovskite material, electronic transport properties was also investigated. Fig.6 represents the temperature-dependent resistivity curves for Mn_3Ga(Ge, Si)N compounds. For Mn_3GaN, the resistivity first increases slowly with increasing temperature, then increase abruptly at 315K, and finally the increasing rate becomes slow with further increasing temperature. However, there always found a drastic drop of the resistivity, not a jump for other materials[12] near the transition temperature. In general, It was thought that there are three parts contributed to the resistivity of magnetic metal. The first term is related to impurity or lattice defects, it is not temperature-dependent, the second term is from the lattice scattering, and the last term is from magnetic moments contribution, which increases with increasing temperature. Deduced from our experimental results, it is the magnetic scattering playing a main role for the upturn of the resistivity. In PM state, the orientation of the magnetic moments becomes disordered and the transport electrons suffer larger scattering probability than that in the AFM state. As a consequence, the mean free path of electrons becomes shorter and the resistivity increases rapidly[23].

For $Mn_3Ga_{0.5}Ge_{0.37}Si_{0.13}N$, the resistivity first increases with temperature up to 320 K, then the resistivity starts to decrease slowly. The phenomenon may be correlated to the shift of the Fermi energy surface due to the AFM-PM transition. A small shift of the Fermi energy surface can result in an increase of the electronic density of state (DOS) near the Fermi level, which could lead to an increase of the effective number of conduction electrons. Correspondingly, the resistivity decreases at

the transition temperature. There is a broader minimum near 360 K, and after 390 K the resistivity increases quickly, which exhibiting typical metallic character.

However, the measured transition temperature for resistivity was always lowered than the observed transition temperature for structure and magnetism. The studies are ongoing for clarifying the reasons and mechanism.

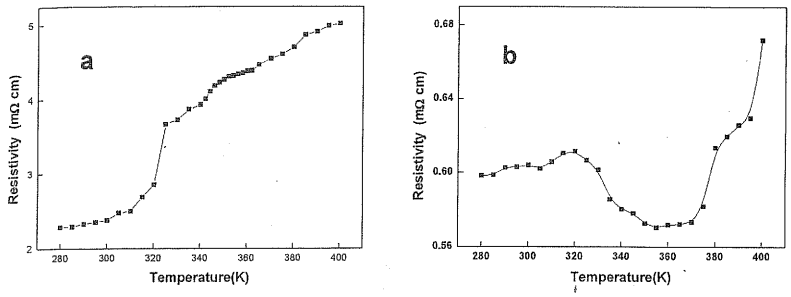

Fig.6 Temperature dependence of resistivity of the samples
(a: Mn_3GaN, b: $Mn_3Ga_{0.5}Ge_{0.37}Si_{0.13}N$)

Conclusion

The crystal structure of $Mn_3Ga(Ge,Si)N$ was analyzed by X-ray diffraction. The thermal expansion coefficient of $Mn_3Ga_{0.5}Ge_{0.37}Si_{0.13}N$ is about $\alpha = -2.8\times10^{-5}$ /K (350K-423K). Partial substitution of Ga by Ge in Mn_3GaN, has changed the discontinuous contraction into continuous. The NTE effect acts in accord with the magnetic transition from AFM to PM. The temperature dependence of resistivity was correspondingly changed. Heat capacity C_p analysis indicated that there is a a qualitative change for the first-order transition occurred in Mn_3GaN after Ge introduced.

Acknowledgements

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