NUKLEONIKA 2013;58(1):149–152

ORIGINAL PAPER

Study of B8-type solid solutions of Al and Si in manganese antimonide

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Abstract. The $Mn_{1.1}Sb_{1-y}Al_y$ ($0 \le y \le 0.2$) and $Mn_{1.1}Sb_{1-y}Si_y$ ($0 \le y \le 0.1$) solid solutions with the B8-type of crystal structure were obtained. The magnetic measurement revealed that the partial substitution of Sb atoms by Al or Si practically do not affect the specific magnetization and Curie temperatures. Mössbauer data showed the local redistribution of atoms in solid solutions by comparison with that in the parent $Mn_{1.10}Sb$.

Key words: B8-type structure • manganese antimonide • Mössbauer effect

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Received: 5 July 2012
Accepted: 14 September 2012

Introduction

Solid solutions on the basis of manganese antimonide with B8-type of crystal structure have important commercial applications as materials for magnetooptics, electrode materials, temperature-sensitive elements [3, 7–9]. That is why the tendency for producing new materials on the basis of manganese antimonide and investigation of their physical properties still persists. The solid solutions with varying magnetic properties were obtained in our previous work: 1) $Mn_{1.1-x}Cu_xSb$ and $Mn_{1.1-x}Zn_x$ Sb with $x \le 0.10$ prepared by the conventional melting method [5] and 2) $Mn_{1.5-x}Cu_xSb$ ($x \le 0.30$) and $Mn_{1.5-x}Zn_xSb$ ($x \le 0.10$) prepared using the high-pressure high-temperature processing. This technique ensures an increase in copper content to 30 at.%, but does not influence zinc content [2].

The purpose of the present work was to determine the solubility region of Al and Si in manganese antimonide with B8 type of crystal structure and to investigate the effect of substitution on the local structure and magnetic properties.

Experimental

The procedure of preparation of MnSb(Al) and MnSb(Si) solid solutions was similar to that described in [5] for $Mn_{1.1-x}Cu_xSb$ and $Mn_{1.1-x}Zn_xSb$. It included slow (during 24 h) heating of a homogeneous mixture of the appropriate quantities of spectroscopically pure initial components in silica tubes with an

Table 1. Lattice parameters (a, c) and Curie temperatures (T_C) for the B8-type solid solutions of Al and Si in manganese antimonide

Sample	a (Å)	c (Å)	c/a	T_C (K)
$Mn_{1.1}Sb$	4.157	5.757	1.385	498
$Mn_{1.1}Si_{0.1}Sb_{0.9}$	4.167	5.742	1.377	470
$Mn_{1.1}Al_{0.1}Sb_{0.9}$	4.177	5.734	1.372	465

inner pressure of 10^{-3} torr up to alloying temperature T = 900–950°C. Next, the mixture was alloyed at T = 900–950°C during 4 h, slowly cooled (during 4–5 h) from 950°C down to 840–860°C (the temperature of B8-phase formation), annealed at T = 840–860°C during 24 h and water quenched. At first, the quantities of initial components were taken in accordance with the chemical formula $Mn_{1.1-x}Al(Si)_xSb$, but it appeared not possible to obtain the solid solution with B8-type structure in the system in such a way. Solid solution of B8-type formed was only in the case when the quantities of initial components were taken in accordance with the chemical formula $Mn_{1.1}Sb_{1-y}Al(Si)_y$. Al or Si atoms replaced Sb atoms in anion sublattice.

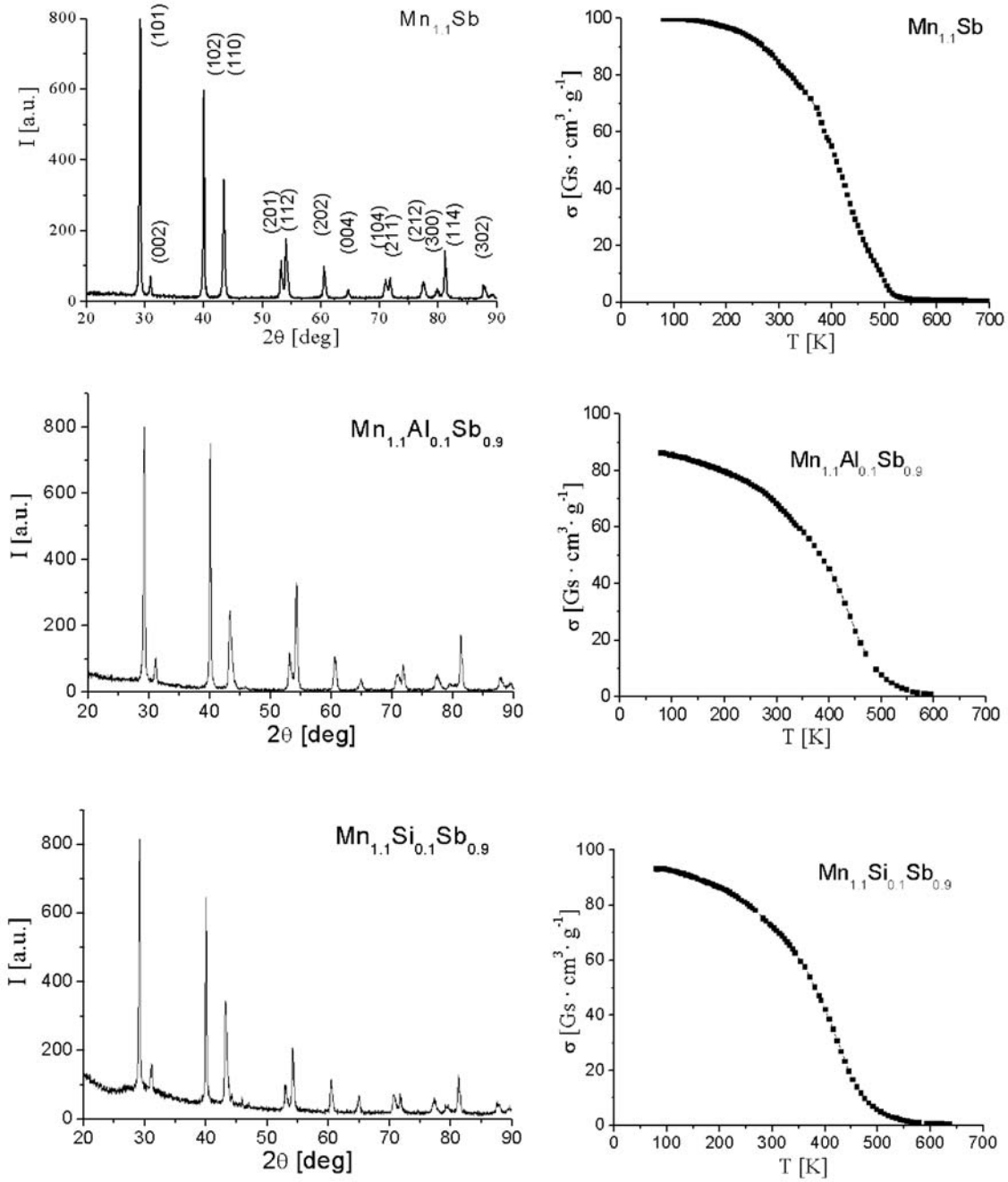

Fig. 1. X-ray diffraction patterns and specific magnetization as a function of temperature for the $Mn_{1.1}Al_ySb_{1-y}$ and $Mn_{1.1}Si_ySb_{1-y}$.

Results

The products of each synthesis were analyzed for the phase composition by powder X-ray diffraction (XRD) analysis and unit cell dimensions were obtained in the same way. The XRD patterns were adjusted by the Rietveld method [4]. Specific magnetization and saturation magnetization were measured in the field of 8.6 kOe and temperature region 77 K – 700 K for all the samples, Table 1. X-ray diffraction patterns and specific magnetization as a function of temperature for the $Mn_{1.1}Al_ySb_{1-y}$ and $Mn_{1.1}Si_ySb_{1-y}$ are shown in Fig. 1.

The solubility region was determined for B8-type solid solution of MnSb-Al and MnSb-Si systems. It is $0 \le y \le 0.2$ for $Mn_{1.1}Sb_{1-y}Al_y$ and $0 \le y \le 0.1$ for $Mn_{1.1}Sb_{1-y}Si_y$.

The magnetic measurements revealed that the partial substitution of Sb atoms for Al or Si practically did not influence the specific magnetization and Curie temperatures.

To gain more detailed insight into the microstructure and magnetic properties of the solid solutions obtained they were characterized by Mössbauer spectroscopy. The experiment was held at room temperature (293 K) in transmission geometry, the gamma source used was ^{57}Fe(Rh). Mn atoms in each sample were partly substituted by the Mössbauer isotope ^{57}Fe during synthesis (2 at.%). XRD analysis showed no appreciable structure difference between the samples with a ^{57}Fe isotope addition and those without it. Hyperfine interactions parameters were refined by computer fitting. Room-temperature Mössbauer spectra are shown in Fig. 2, the fitting parameters are listed in Table 2. Firstly, we supposed that substitution of the metalloid atoms (Sb) by Al and Si would not influence the main ^{57}Fe hyperfine interaction parameters and the shape of Mössbauer spectra of solid solutions should be close to that of $Mn_{1+x}Sb$.

In fact there is a significant difference in the spectrum structure. The spectrum for $Mn_{1+x}Sb$ consists of two sextets. Our previous Mössbauer study of the $Mn_{1+x}Sb$ and the MnSb(Cu,Zn) [6] confirmed that there are two types of magnetically non-equivalent positions of metal atoms in such a type of solid solutions. First, this presentation corresponded to the essentialities of B8-type structure, where metal atoms (including Fe) are located in two types of structural non-equivalent positions, octahedral and trigonal bipyramidal. Second, neutron diffraction results obtained for $Mn_{1+x}Sb$ [1] revealed two different values of the magnetic moment of metal atom in $Mn_{1.10}Sb$. This also argues for two different values of hyperfine magnetic field at Fe atoms. As the magnetic moment of the metal atom in octahedral position is 3.6 μ_B and 3.0 μ_B for the atom in interstitial position [1], we suppose that the subspectrum with a larger B_{eff} value in each spectrum B_{eff} corresponds to Fe atoms in regular octahedral positions. The subspectrum with a smaller B_{eff} value in each solid solution spectrum was attributed to the metal atoms in trigonal bipyramidal sites. Using the two sextet model described in [2, 6], we obtained a good fitting results for the $Mn_{1+x}Sb$ spectrum and those for B8-type solid solutions of Cu or Zn in $Mn_{1+x}Sb$.

Both Al and Si solid solution spectra consist of two magnetic subspectra with the field values similar to those at ^{57}Fe in the parent $Mn_{1.10}Sb$. Beside sextets, there

Table 2. Hyperfine interactions parameters derived from room-temperature Mössbauer spectra of B8-type solid solutions of Al and Si in manganese antimonide; IS – isomer shift relative to α-Fe, QS – quadrupole splitting, B_{eff} – hyperfine magnetic field, Γ – HWHM

Sample	Subspectrum 1				Subspectrum 2				Subspectrum 3			
	IS (mm/s)	QS (mm/s)	B_{eff} (T)	Γ (mm/s)	IS (mm/s)	QS (mm/s)	B_{eff} (T)	Γ (mm/s)	IS (mm/s)	QS (mm/s)	Γ (mm/s)
$Mn_{1.08}Fe_{0.02}Sb$	0.386(2)	–0.198(2)	6.07(1)	0.178(3)	0.438(4)	0.108(3)	8.28(2)	0.161(5)	–	–	–
$Mn_{1.08}Fe_{0.02}Si_{0.1}Sb_{0.9}$	0.397(7)	–0.288(2)	5.86(5)	0.19(fix)	0.42(3)	–0.200(9)	8.5(2)	0.19(fix)	0.141(2)	0.35(2)	0.174(fix)
$Mn_{1.08}Fe_{0.02}Al_{0.1}Sb_{0.9}$	0.473(5)	–0.368(6)	5.07(3)	0.19(fix)	0.78(9)	–0.243(5)	6.3(5)	0.19(fix)	0.339(6)	0.46(8)	0.174(fix)

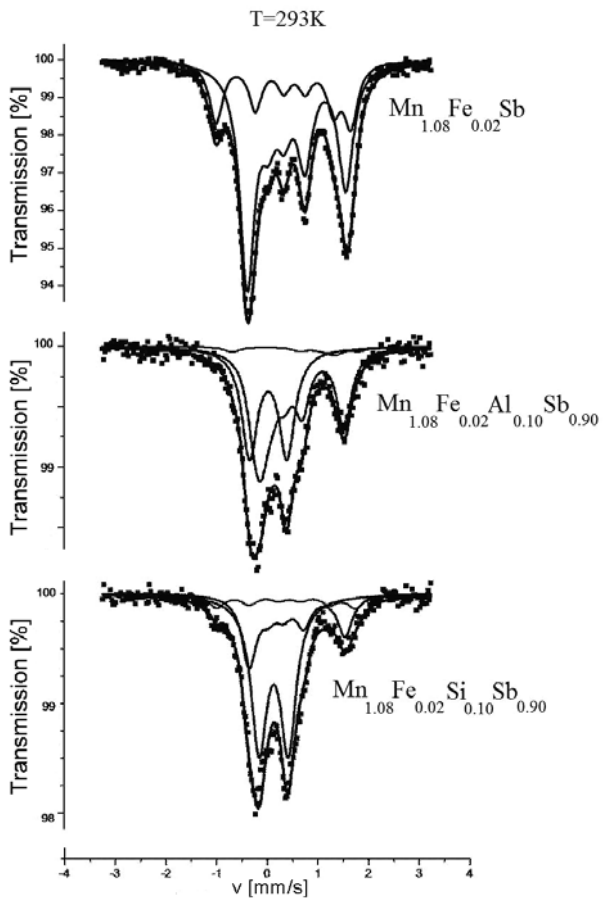

Fig. 2. Room-temperature Mössbauer spectra for the $Mn_{1.1}Al_ySb_{1-y}$ and $Mn_{1.1}Si_ySb_{1-y}$.

is a quadrupole doublet with an ambiguous nature in the spectra of solid solutions studied. We supposed that the most probable reason of this is a local redistribution of atoms. Sb atoms form the nearest neighborhood of each octahedral metal atom – Mn or Fe. If we suppose that Si or Al atoms replace Sb ones then the metal atoms (Mn or Fe) fall out of the magnetic interactions as this interaction is realized in the form of indirect exchange between them via Sb and thus blocked. The fact that the relative area of the sextet with the higher B_{eff} in each spectrum is smaller than the relative area of the sextet with the lower B_{eff} argues for this supposition.

Conclusions

The nature of a quadrupole doublet needs to get proper understanding because the magnetic measurements detected no appreciable weakening of magnetic interactions in the solid solutions in comparison with those in the parent $Mn_{1.10}Sb$ (Fig. 1). The local redistribution of the atoms that follows from the Mössbauer data could affect the electrical properties of solid solutions obtained and hereby the present work sets the problem for further study.

The solid solutions $Mn_{1.1}Sb_{1-y}Al_y$ with $0 < y \le 0.2$ and $Mn_{1.1}Si_{0.1}Sb_{0.9}$ with B8-type of crystal structure were obtained. The magnetic measurement revealed that the partial substitution of Sb atoms for Al or Si nearly do not affect the specific magnetization and Curie temperatures. The Mössbauer spectroscopy data showed the local redistribution of atoms.

References

1. Bouwma J, Van Bruggen CF, Haas C, van Laar B (1971) Neutron diffraction and magnetic properties of $Mn_{1+x}Sb_{1-y}Sn_y$. J Phys C 32:C1-78–C1-80
2. Budzyński M, Mitsiuk VI, Ryzhkovskii VM, Surowiec Z, Tkachenko TM (2010) Preparation and properties of $Mn_{1.5-x}Cu_xSb$ and $Mn_{1.5-x}Zn_xSb$ solid solutions with the B8 structure. Inorg Mater 46:1049–1053
3. Ionica CM, Lippens PE, Fourcade JO, Jumas JC (2005) Study of Li intertion mechanisms in transition metal antimony compounds as negative electrodes for Li-ion battery. J Power Sources 146:478–481
4. McCusker LB, Von Dreele LD, Cox DE, Louer D, Scardi P (1999) Rietveld refinement guidelines. J Appl Crystallogr 32:36–50
5. Mitsiuk VI, Rizhkovskii VM, Tkachenka TM (2009) Structure and magnetic properties of MnSb(Zn) and MnSb(Cu) solid solutions. J Alloys Compd 467:268–270
6. Mitsiuk VI, Ryzhkovskii VM, Tkachenka TM (2007) Magnetic material. Belarusian Patent no. 11937
7. Mitsiuk VI, Ryzhkovskii VM, Tkachenka TM (2008) Effect of Cu and Zn substitutions on MnSb properties. AIP Conf Proc 1070:64–68
8. Mitsiuk VI, Ryzhkovskii VM, Tkachenka TM (2008) Magnetic material. Belarusian Patent no. 13034
9. Thackeray MM, Vaughey JT, Johnson CS *et al.* (2003) Structural considerations of intermetallic electrodes for lithium batteries. J Power Sources 113:124–130