Study on Diluted Magnetic Semiconductors $Zn_{1-x}Mn_xB$ (B = S, Se) : Synthesis and Structural Characterization

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(Received: Feb. 19, 1997 Accepted: Mar. 21, 1997)

Abstract

A sintering technique has been successfully employed to synthesize the diluted magnetic semiconductors of the type $Zn_{1-x}Mn_xB$ (B = S, Se) in the concentration range $0.1 \leq x \leq 0.5$. From the structural study by x-ray diffraction, it is found that the present synthesis technique is much more superior to a modified Bridgmann method or even the conventional sintering method in yielding homogeneous product. Changes in the lattice constants due to the addition of Mn are studied in detail.

1. Introduction

The semiconducting materials whose lattices are made up in part of substitutional magnetic atoms, commonly known as diluted magnetic semiconductors (DMS), have attracted wide attention due to their remarkable electronic, magnetic and optical properties[1]. Of late the interest in these has revived because of their important applications in the construction of low-dimensional electronic systems[2]. The alloying of the elements makes it possible to vary continuously the physical characteristics of these materials such as energy gap, conductivity, magnetic moment and many other important properties. Since electronic features of an alloy after the addition of an impurity depend very strongly on the rearrangement of atoms, characterization of atomic structure, especially the change of atomic distance as a function of concentration of the impurity becomes very crucial. In this article, successful synthesis of the $Zn_{1-x}Mn_xB$ (B = S, Se) series, in the concentration range of Mn $0.1 \leq x \leq 0.5$, is described. The change of the lattice constants observed by X-ray diffraction is discussed.

2. Synthesis of Semiconductors by Solid State Diffusion

In the present study, a careful sintering technique based on solid state diffusion is employed to synthesize the $Zn_{1-x}Mn_xB$ (B = S, Se) series with different Mn concentrations. It has been reported that a modified Bridgmann method causes the inhomogeneous distribution of the constituents (ZnB and MnB) in the final product. This is mainly because of the vast difference in their melting points (e.g. wurtzite form of ZnS melts[3] at 1850 C at 150 atm. MnS (green) melts at 1600 C, MnSe at[4] 1460 C). The existence of significant dissociation pressure also makes it difficult to control the desired concentration when such melt growth technique is employed.

Pure fine powder (99.999%, 300 mesh) of ZnS and MnS for the former series and ZnSe and MnSe for the latter series were weighed in the stoichiometric proportions to an accuracy of 1mg and were hand mixed in agate mortar. Further mixing was not needed as one of the ingredients was volatile and sufficient time made it possible for the ingredients to diffuse homogeneously.

A 10cm long transparent quartz tube (i.d. 10mm and o.d. 13mm) was sealed at one end by oxygen-hydrogen torch flame to make an ampoule and the mixtures mentioned above were transferred into the ampoules. To prevent suction of fine powder while evacuation as well as excessive heating during sealing sintering, silica wool was inserted on top of the mixtures. Long narrow capillaries were drawn just above the wool and the open end of the ampoules was connected to a vacuum system to get vacuum better than 10^{-6} Torr. The capillaries were sealed while the system was still running.

A computer controlled furnace (KDF S70 ; Denken, Japan) was used for the sintering. The variation of temperature was ±0.5 C even at 1000 C. Further, the furnace has a long and even hot zone. For the $Zn_{1-x}Mn_xS$ series the evacuated ampoules were heated to 850 C at the rate of 20 C per hour and were kept for 72h,

while for the $Zn_{1-x}Mn_xSe$ series the sintering temperature was 1000°C , with the heat up rate of 20°C per hour and the holding time of 36h. The color of $Zn_{1-x}Mn_xS$ samples changed from light cream to orange progressively as the concentration of Mn was increased from x = 0.1 to 0.5, while the $Zn_{1-x}Mn_xSe$ were found to vary from yellow to reddish.

3. Structural Studies by X-ray Diffraction

The x-ray diffraction measurements were carried out using K_β filtered Cu x-radiation from Rigaku rotating anode x-ray generator (RINT) operated at 40kV and 200mA. A wide angle goniometer equipped with 1 degree divergence and scattering slits, and 0.15mm receiving slit was used. The typical powder patterns are shown in Fig 1. It has been found that the $Zn_{1-x}Mn_xS$ are wurtzite type while the $Zn_{1-x}Mn_xSe$ are diamond for Mn concentration x = 0.1 and 0.2, and are wurtzite for x = 0.35, 0.4 and 0.5. The lattice constants obtained through the Cohen's least squares method are listed in Table 1. It is found that both series essentially follow the Vegard's law. As for $Zn_{1-x}Mn_xS$, the lattice expands only in the plane and the change is 1.7%, while the off plane axis variation is within only 0.03%.

In order to study the change in lattice constants in detail we have plotted in Fig 2 the variations in the distance between cations (Zn or Mn) as a function of the Mn concentration. Since there occurs a structural change from diamond to wurtzite for $Zn_{1-x}Mn_xSe$, the lattice constants can be unified considering the geometrical

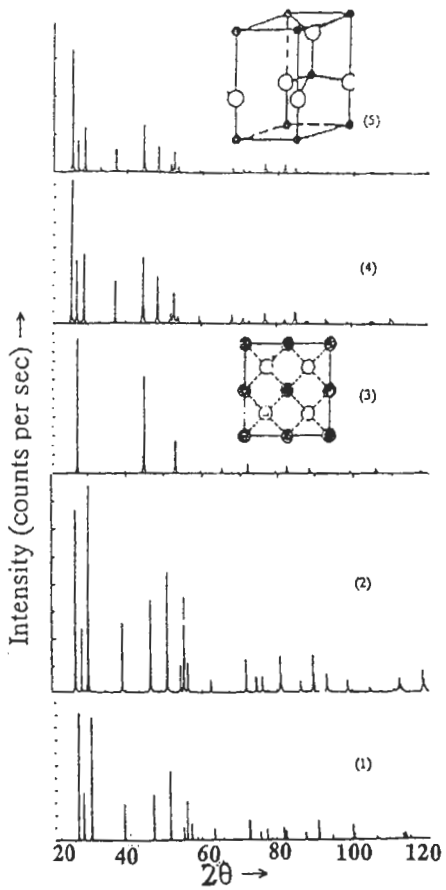

Fig. 1 X-ray diffraction patterns obtained for (1) $Zn_{0.9}Mn_{0.1}S$, (2) $Zn_{0.5}Mn_{0.5}S$, (3) $Zn_{0.9}Mn_{0.1}Se$, (4) $Zn_{0.65}Mn_{0.35}Se$, (5) $Zn_{0.5}Mn_{0.5}Se$. Their crystal structure is also illustrated in the figure as inset with black solid circles as Zn atoms and hollow circles as S or Se.

Table 1 Summary of the lattice constants obtained for ZnMnB (B = S, Se)

Compound	Mole % of Mn(*)	a [Å]	c [Å]	c/a
ZnMnS-1	10	3.8377	6.2891	1.6388
ZnMnS-2	20	3.8473	6.2883	1.6345
ZnMnS-3	30	3.8775	6.313	1.6281
ZnMnS-4	40	3.8932	6.3306	1.6261
ZnMnS-5	50	3.9024	6.3116	1.6174
ZnMnSe-1	10	5.6902		
ZnMnSe-2	20	5.7056		
ZnMnSe-35	35	4.06	6.6625	1.64
ZnMnSe-4	40	4.077	6.662	1.634
ZnMnSe-5	50	4.0895	6.6565	1.6277

(*) The formula unit is $Zn_{1-x}Mn_xB$ (B = S, Se).

While ZnMnSe-1 and ZnMnSe-2 are diamond type lattices the rest have wurtzite type structure.

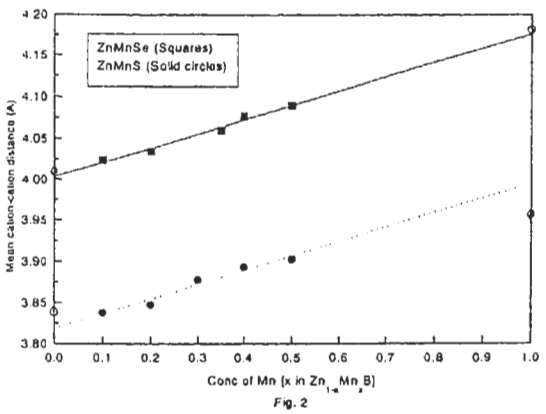

Fig. 2 Dependence of the cation-cation distance, dc ($d_c = a_o/\sqrt{2}$ in the diamond type lattice and d_c = a or $c/\sqrt{(8/3)}$ in the wurtzite type lattice) on the Mn concentration, x in the $Zn_{1-x}Mn_xB$ (B = S, Se). The open circles at the ends of the least squares fit lines represent the data obtained by previous workers (Ref. 7 and 8)

relation governing the cation-cation distance. The reliability of the present results can be confirmed if the plots are extrapolated to reach the constituents at the ends. From Fig.2, the extrapolated cation-cation distances at x = 0 are found to be 3.819Å and 4.004Å for $Zn_{1-x}Mn_xS$ and $Zn_{1-x}Mn_xSe$, respectively. Similar extrapolation to x = 1.0 would give the distances to be 3.994Å and 4.176Å for the respective series. These results are in excellent agreement with those due to Wyckoff[5] based on his precise determination on single crystals as well as those by Van Vechten et al.[6] based on their quantum mechanical calculations. This suggests that the present synthesizing procedure using a sintering technique is successful to control the microscopic structure. The earlier studies on the materials prepared by a modified Bridgmann method[7] or even the conventional sintering method[8] have not given the reasonable lattice constants

It is interesting to study the reason why the lattice is expanding only in the plane and the distance between cation (Zn or Mn) and anion (S) remains unchanged for $Zn_{1-x}Mn_xS$. To understand such detailed atomic structure around a specific atomic species, X-ray absorption fine structure (XAFS) is promising[9] and therefore both Zn and Mn K XAFS study would throw some light on this problem and enable to bring forth some quantitative discussion. Our preliminary Mn K XAFS studies using the NRIM Super XAFS facility[10]

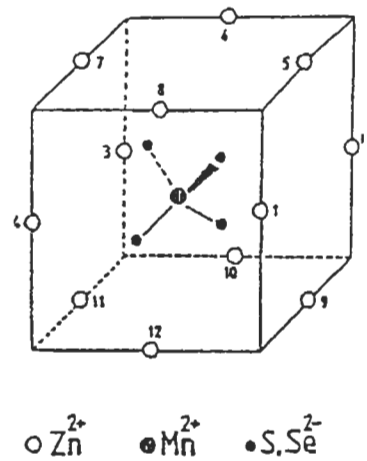

Fig. 3 Proposed local structure model around Mn for $Zn_{1-x}Mn_xB$ (B = S, Se).

have shown that Mn is four fold coordinated by S atoms, but has the distance between cation (Mn) and anion (S) different from the present diffraction study. Further studies are now in progress.

4. Summary

In a nutshell we have observed that a sintering technique is useful for the preparation of $Zn_{1-x}Mn_xB$ (B = S, Se) wherein one of the ingredients is volatile. The technique is much more superior to a modified Bridgmann method or even the conventional sintering method in the capability of getting the homogeneous product. ZnS-MnS system forms wurtzite type compounds at least up to x = 0.5, while there occurs a phase change, from diamond type to wurtzite type, in the ZnSe-MnSe system. The lattice constants obtained are highly accurate as the microscopic structure of the ingredients deduced from these values are in excellent agreement with standard reliable references. The lattice of $Zn_{1-x}Mn_xS$ is found to expand only in the plane as the distance between cation (Zn or Mn) and anion (S) remains unchanged.

Acknowledgments

One of the authors (SDD) wishes to acknowledge gratefully the Post Doctoral Research Award by the Japan Society for Promotion of Science, and expresses deep sense of gratitude to Professor I. Nakai of Science University of Tokyo for his continuous encouragement. The authors are thankful to the staff of the National Research Institute for Metals, Tsukuba for their kind assistance during

the experiment. The authors are benefited greatly by stimulating discussions with Dr. Claude Landron, CNRS, France.

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