PRECIPITATES IN $Cd_{1-x}Ni_xSe$ CRYSTALS GROWN BY THE BRIDGMAN METHOD

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Single crystals of $Cd_{1-x}Ni_xSe$ alloys (x ranging from 0 to 0.075) were investigated using electron microprobe and X-ray diffraction. The analysis shows the presence of Ni–Se precipitates. The solubility limit of Ni is estimated to be 0.008.

PACS numbers: 61.70.Wp, 61.55.Hg, 81.10.Fq

1. Introduction

The research on diluted magnetic semiconductors (DMS) representing a special class of semiconducting single crystals with some unique physical properties has been focused mainly on Mn-based alloys [1, 2]. Recently, properties of Fe, Co and Ni based alloys have also been investigated (see [2–6] and references therein).

As it is well established, II–Mn–VI mixed crystals can be grown in a wide range of Mn content. II–VI compounds containing other magnetic ions such as Fe and Co do not form just a simple extension of the Mn-based family. For example, the solubilities of Fe and Co are far below the solubility of Mn [2]. In addition to the development of II–Fe–VI and II–Co–VI alloys there is a progress in II–VI ternary alloys containing Ni. Crystals of $Zn_{1-x}Ni_xSe$ and $Zn_{1-x}Ni_xS$ have only recently been prepared by chemical vapour technique, and so far, very little information about them is available [6, 7]. In view of the above, it seems worthwhile to examine the structural characteristics of $Cd_{1-x}Ni_xSe$ alloys.

2. Experimental

Single crystals of $Cd_{1-x}Ni_xSe$ alloys were grown by the vertical Bridgman technique. The melting point of pure CdSe (1264°C) is still sufficiently low to use quartz ampoules. Double thick-walled ampoules were used throughout the study. Pure Ni (6N) and presynthesized polycrystalline CdSe obtained from high-purity

elements were used as starting materials. The prepared mixture was placed in a slightly tapered silica ampoules covered with a transparent graphite coating to prevent sticking of the material to the quartz wall. The ampoule was then sealed off in a vacuum better than 10^{-6} torr. The doubled capsule was placed in a furnace at the temperature-gradient zone of about $10°C/cm$. The temperature of the charge was slowly raised from 600 to 1300°C. The capsule was held at 1300°C for about 5 hours to homogenize the melt and then lowered through the furnace at a speed of, typically, 3 mm/h.

The electron-probe microanalysis (EPMA) was carried out using a JEOL JXA-50A scanning microscope equipped with an automated LINK system for energy-dispersive X-ray analysis. The observations included COMPO (backscattered electrons image in atomic number contrast mode), X-ray area scans (mapping of distributions of characteristic X-ray lines), WD (wavelength dispersive) EPMA and ED (energy-dispersive) EPMA. In the latter two methods, intensities of characteristic X-ray lines are measured and evaluated to give chemical compositions of samples, on local scale. The X-ray diffraction patterns were obtained on powders, with anautomated DRON diffractometer and interpreted using DHN-PDS and SCANIX [8] packages.

3. Results

The composition of the samples was examined using the energy dispersive X-ray fluorescence (ED XRF) measured for a large area of the investigated sample. The results presented in Table I show the general tendency of increase in averaged

TABLE I

Chemical analysis of $Cd_{1-x}Ni_xSe$. Precipitate dimensions concern the section perpendicular to the growth direction.

Sample	Nominal composition (x)	ED XRF $x_{average}$	Matrix WD EPMA x_{matrix}	Precipitate dimensions $[\mu m]$
P432	0.005	0.002	0.0085	not observed
P416	0.010	0.010	–	5–40
PX	0.021	–	0.0075	5–40
P431	0.030	0.060	0.0081	15–20
P459	0.075	0.080	0.0028	15–20

Ni content according to the nominal composition. The discrepancies related to the nominal composition are due to low accuracy of this method and probably to inhomogeneities of the samples.

For samples of $x \geq 0.01$ the scanning electron microscopy performed at planes perpendicular to the growth direction reveals presence of circular precipitates (see Fig. 1). The number of precipitates increases with x. Their dimensions
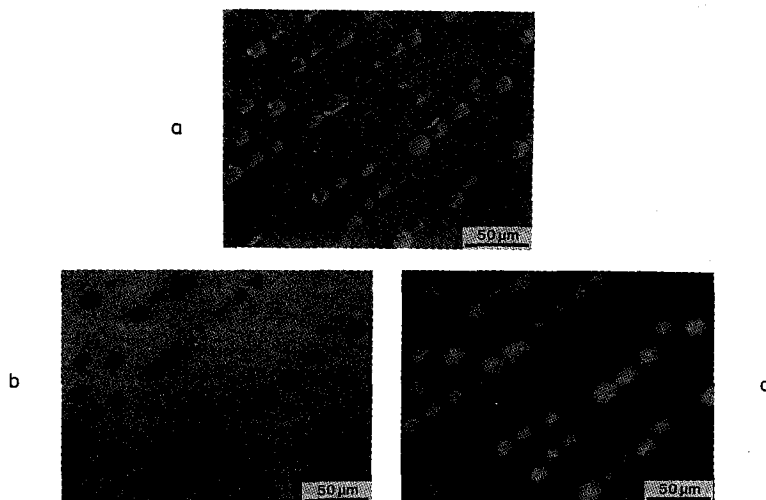
Fig. 1. (a) COMPO (atomic number contrast) image of the sample $Cd_{0.925}Ni_{0.075}Se$. The NiSe precipitates are visible. (b) and (c) X-ray area scans of the same sample; lines Cd L_{α_1} (b) and Ni K_{α_1} (c).

varied in the range 5–40 μm (see Table I). In the sample of the highest Ni content (P459) the chains of precipitates were observed. The composition of the precipitates was determined to be NiSe.

The composition of the matrix was investigated using wavelength-dispersion electron-probe microanalysis (WD EPMA) method. The results presented in Table I show that in 3 among 4 samples the Ni content in the matrix was about $x = 0.008$. The low Ni content in the sample P459 is probably due to the inhomogeneity.

X-ray diffraction measurements reveal the presence of NiSe phase for samples P431 and P459. The values of the lattice constants of the $Cd_{1-x}Ni_xSe$ matrix are presented in Table II.

4. Discussion

On the basis of the applied methods it may be concluded that Ni atoms substitute Cd atoms in $Cd_{1-x}Ni_xSe$ for $x < 0.008$. It is interesting to note that this solubility limit decreases in the sequence Mn–Co–Fe–Ni in Cd–Se compounds: Mn 50% [2], Co 22% [2], Fe 15% [2], Ni 0.8% (this work).

The variation of lattice parameters with composition within the solubility range is comparable to the error of the lattice parameter calculation. Therefore, the composition of the matrix in the case of our samples could not be investigated with this method.

The limit of detection of the NiSe phase by X-ray diffraction is estimated to be about 1.5 vol.% (which corresponds to nominal x about 0.025). We note

TABLE II

Lattice constants for the matrix wurtzite phase in $Cd_{1-x}Ni_xSe$.

Sample	a [A]	c [A]	NiSe
pure CdSe	4.299 ± 0.001	7.012 ± 0.003	–
P432	4.299 ± 0.002	7.011 ± 0.002	–
P416	4.299 ± 0.002	7.006 ± 0.005	–
PX	4.298 ± 0.001	7.008 ± 0.003	–
P431	4.300 ± 0.001	7.014 ± 0.003	+
P459	4.299 ± 0.002	7.005 ± 0.003	+

that this limit is dependent on the X-ray equipment and on the sample quality. Using EPMA modes (COMPO, X-ray scan and WD EPMA), the NiSe phase was detected at nominal $x = 0.01$.

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