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Growth of (Cd, Mn)GeP_2 ferromagnetic semiconductor

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Abstract

Two-step synthesis for polycrystalline bulk growth of a solid solution based on the $CdGeP_2$ ternary compound is reported. Transition metal Mn was used as a chemical partner for the solid solution of a new semiconductor material (Cd, Mn)GeP_2, which shows ferromagnetic properties. X-ray diffraction revealed a chalcopyrite crystal structure with a small change in the lattice parameter due to the Mn-content. The elevated concentration of the transition d-element (50%) leads to extraction of the MnP secondary phase. All the Mn-containing polycrystalline phases (Cd, Mn)GeP_2 showed a classic magnetization dependence on temperature and a magnetic hysteresis loop up to room temperature. The Curie temperature of polycrystalline (Cd, Mn)GeP_2 was measured as 310 K, which is slightly lower than that of the single crystal phase. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

For a rather long period of time no new compounds appeared in the chalcopyrite family of II–IV-V_2 materials [1]. Recently, we showed that incorporation of an elevated concentration of manganese into the host $CdGeP_2$ single crystal results in creating a new ferromagnetic material (Cd, Mn)GeP_2 with a chalcopyrite crystal structure [2,3]. Herein, the two-step synthesis for bulk growth of a polycrystalline solid solution based on $CdGeP_2$ ternary compound is reported. Crystal structure and magnetization properties are described as well.

2. Experimental procedure

Pure chemicals as Cd grains–5 N, Ge grains–4 N, P chunks–5 N, Mn flakes–3 N were used as starting components. A cylindrical furnace with a quartz reactor and thermocontroller CHINO model KP was employed for the growth. The crystal structure and chemical composition were measured with Rigaku RAD-IIC X-ray diffractometer (XRD), scanning electron microscope (SEM) Hitachi S-4500 supplied with

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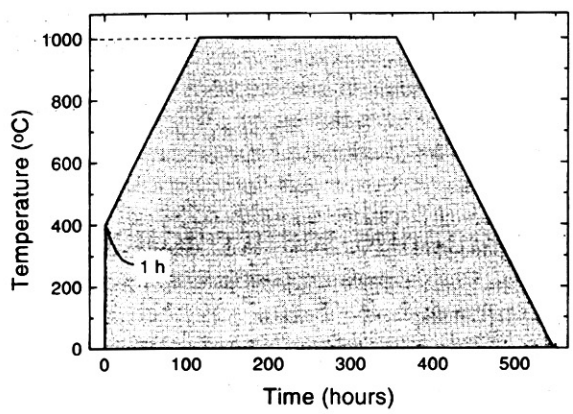

Fig. 1. Temperature program of the furnace for synthesis of $CdGeP_2$ polycrystalline bulk.

EMAX-5770 instrument using EDX and FE-SEM techniques. Magnetization effect was measured using a vibrating sample magnetometer (VSM) with temperature control in the range of 80–350 K.

3. Technology and characterization

The first step of the material preparation included a direct fusion of Cd, Ge and P starting chemical components taken in the stoichiometric composition. A small amount of iodine (1 mg/cm^3) as a transporting agent was added in the evacuated

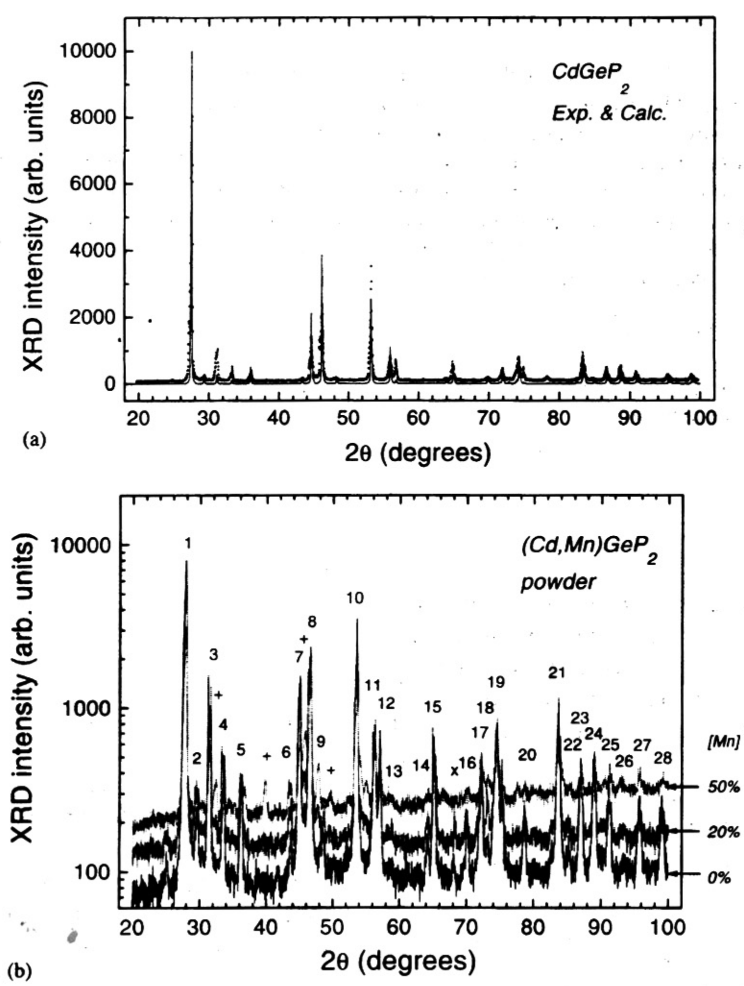

Fig. 2. X-ray diffraction spectra of $CdGeP_2$ and $(Cd, Mn)GeP_2$ polycrystals. (a) Comparison of experimental and calculated spectra, (b) comparison of substances with various Mn-concentration.

quartz ampoule together with mixed starting components (5 g charge in average). Heating by program up to 1000°C was performed for 360 h (Fig. 1). The second step of preparation consisted of addition of Mn element in different mole fraction (20% and 50%) followed by thermal treatment in N_2-gas flowing open system at 500°C for 2 h. Homogeneous bulk ingots were grown after both steps in the reaction zone.

SEM images of the prepared powder samples gave a rather uniform distribution for Cd and Ge species over the surface. Whereas, Mn and P elements are distributed less uniformly in the sample with 50% Mn-content. A precipitation of a secondary phase composed of Mn and P is expected for the sample with 50% Mn-content.

XRD spectra in Fig. 2 show experimental data for grown $CdGeP_2$ and (Cd, Mn)GeP_2 powders with different Mn-concentration and calculation. Experimental peaks of $CdGeP_2$ polycrystalline substance after the first growth step are in good agreement with calculated XRD spectra of $CdGeP_2$ (Fig. 2(a)). XRD spectrum after the second growth step shows that 20% (Cd, Mn)GeP_2 solid solution is a homogeneous material with a lattice parameter close to the $CdGeP_2$ parent material. The 50% (Cd, Mn)GeP_2 solid solution is basically a chalcopyrite substance with a small amount of MnP second phase. Fig. 2(b) shows chalcopyrite peaks marked by numbers (1–28) and surplus peaks (+) due to binary manganese phosphide arising in Mn-enriched phase only.

Magnetic measurements performed by the VSM technique at temperatures from 80 to 350 K exhibited distinct hysteresis loops for (Cd, Mn)GeP_2 phases in a wide temperature range. Fig. 3 demonstrates M–H curves at low and high temperatures, $T = 123$ and 296 K. At that, 50% material shows the magnetization amplitude about three times as high as 20% solid solution. Pure $CdGeP_2$ powder did not give any ferromagnetic behavior, only a diamagnetic contribution was obtained. The temperature dependence of magnetization for polycrystalline (Cd, Mn)GeP_2 solid solutions gave the Curie temperature at 310 K that is around the same value for the single crystal (Cd, Mn)GeP_2 phase [4]. It is important to note that MnP is a ferromagnetic material with $T_c = 290$ K and it can contribute to magnetization of the quaternary compound with elevated Mn-content at low temperatures. Therefore, VSM measurements were done especially at $T > T_c$ (MnP) to prove that the magnetization effect is owing to just the new chalcopyrite compound. The results in Fig. 3 unambiguously show that the distinct magnetization at room temperature arises from the chalcopyrite material even in the case of 50% [Mn]. An influence of MnP in the Mn-enriched (Cd, Mn)GeP_2 phase is not excluded at all, but we believe it is absent in the 20% (Cd, Mn)GeP_2 phase. For further clarifying the question, a study of chemical interaction between (Cd, Mn)GeP_2 and MnP phases is required that can be carried out via investigation of a quasi-binary cut in this system.

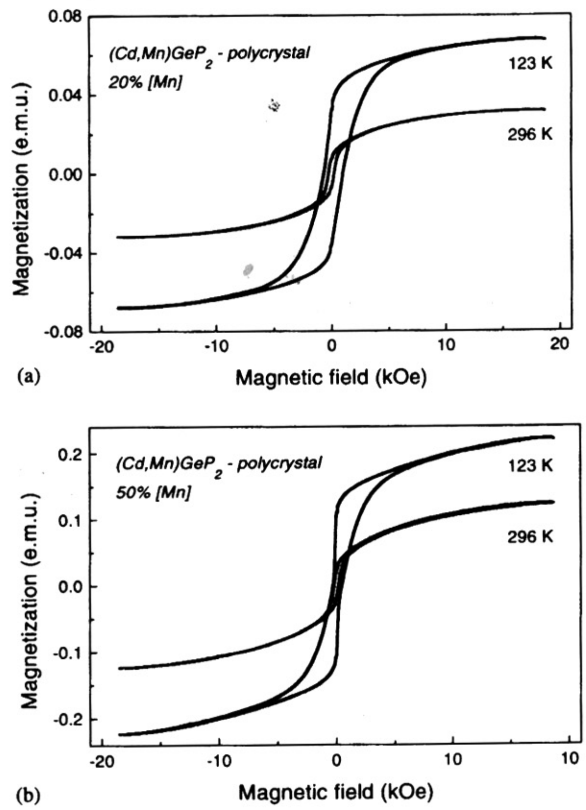

Fig. 3. Magnetic hysteresis loops for (Cd, Mn)GeP_2 polycrystalline samples with Mn-concentration of 20% (a) and 50% (b).

4. Conclusion

We have synthesized for the first time a polycrystalline (Cd, Mn)GeP_2 ferromagnetic material with various Mn contents as 0%, 20% and 50%. The base crystal structure of all the compounds is chalcopyrite. Both Mn-containing materials show the hysteresis loop at room temperature and the Curie temperature of 310 K by VSM measurements. The Mn-enriched phase (50%) displays a small addition of MnP, which could contribute to magnetization at low (<290 K) temperatures. So, high-temperature ferromagnetism is due to (Cd, Mn)GeP_2 chalcopyrite-type compound. The new room-temperature ferromagnetic material can find application in the developing areas of spintronics and magnetoelectronics [5,6].

Acknowledgements

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References

[1] Landolt-Börnstein, in: O. Madelung (Ed.), Semiconductors: Physics of Ternary Compounds, vol. 17h, Springer, Berlin, Heidelberg, 1985.
[2] G.A. Medvedkin, T. Ishibashi, T. Nishi, K. Hayata, Y. Hasegawa, K. Sato, Jpn. J. Appl. Phys. 39 (2000) L949.
[3] G.A. Medvedkin, T. Ishibashi, T. Nishi, K. Sato, Semiconductors 35 (2001) 305.
[4] K. Sato, G.A. Medvedkin, T. Nishi, Y. Hasegawa, R. Misawa, K. Hirose, T. Ishibashi, J. Appl. Phys. 89 (2001) 7027.
[5] G.A. Prinz, Science 282 (1998) 1660.
[6] H. Ohno, J. Magn. Magn. Mater. 200 (1999) 110.