Synthesis and Magnetic and Electrical Study of Tm$_x$Mn$_{1-x}$S Solid Solutions

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Abstract—New antiferromagnetic semiconductor compounds Tm$_x$Mn$_{1-x}$S ($0 \leq x \leq 0.15$) with an NaCl-type FCC lattice are synthesized, and their structural, magnetic, and electrical properties are investigated at temperatures of 80–1100 K in magnetic fields of up to 10 kOe. Anomalies in the temperature dependence of resistivity in the region of magnetic transition are observed. The activation energy of the synthesized compounds is found and shown to grow along with the concentration of a substitute.

INTRODUCTION

The strong interrelation between the electric and magnetic subsystems in some substances is of great interest in the development of matrices of microelectronic devices [1, 2]. The use of such substances allows us to extend the ranges of application of sensor technology and spintronic devices [3]. Promising materials with metal–nonmetal phase transformations and magnetoelectric effect include cation-substituted sulfides Me_xMn$_{1-x}$S (where Me is a 3d metal [4, 5] or Ln [6, 7]), which we have already studied. These sulfides are interesting for fundamental research due to the possibility of studying the metal–dielectric phase transitions, magnetic phase transformations, and magnetoresistive effects that occur upon varying the concentration of rare-earth (RE) thulium ions with variable valence that are substituted for manganese cations.

The investigated compounds are synthesized on the basis of α-MnS monosulfide, a second-type antiferromagnet with a Neel temperature of $T_N = 150$ K and a NaCl-type face-centered cubic (FCC) lattice [8]. Manganese monosulfide is a p-type semiconductor with low hole mobility in the 3d bands, carrier density n^{-18} cm^{-3}, and conductivity activation energy $E_a \sim 0.3$ eV in the paramagnetic state [9].

Thulium monochalcogenides TmX ($X =$ S, Se, or Te) are a group of model objects for studying the interaction between the electrons of the inner and outer shells of RE elements. As the atomic number of a chalcogenide grows, these materials undergo a sequential transition from metal system TmS with a thulium valence of 3+ to the substance TmSe with variable valence 2.75+, and then to TmTe semiconductor with a Tm valence rigidly equal to 2+. At low temperatures, TmS exhibits the properties of a metal concentrated Kondo system. TmX compound has a NaCl-type crystal structure with lattice parameters of $a = 0.5405$–0.5420, 0.5690–0.5710, and 0.6340–0.6385 nm for S, Se, and Te, respectively [10]. The difference between the thulium compounds and other substances with variable valence (Sm, Yb, Ce, and Eu) is that Tm is magnetic in both configurations (2+ and 3+), ignoring the possible role of the crystal field (Tm^{2+} 4f^{13} $^2F_{7/2}$ and Tm^{3+} 4f^{12} $^3H_6$), so at low temperatures, thulium compounds are magnetically ordered and exhibit interesting magnetic field–induced effects.

The aim of this work was to synthesize and investigate the structural, magnetic, and electrical properties of TmS–MnS solid solutions.

EXPERIMENTAL

We synthesized Tm$_x$Mn$_{1-x}$S solid solutions with a $0.01 \leq x \leq 0.15$ concentration of substitute, determined their crystal structure, and established the temperature dependences of magnetic susceptibility and resistivity.

Our Tm$_x$Mn$_{1-x}$S crystals were grown in a quartz reactor from a melt of polycrystalline sulfide powders. The reactor with the charge in glassy carbon crucibles was drawn through the single-turn inductor of a microwave unit. High-purity argon was used as our inert medium [11]. The phase composition and crystal structure of the Tm$_x$Mn$_{1-x}$S samples were determined at 300 K on a DRON-3 diffractometer (CuK_α radiation). Magnetic susceptibility was measured in vacuum using the ponderomotive technique at tempera-
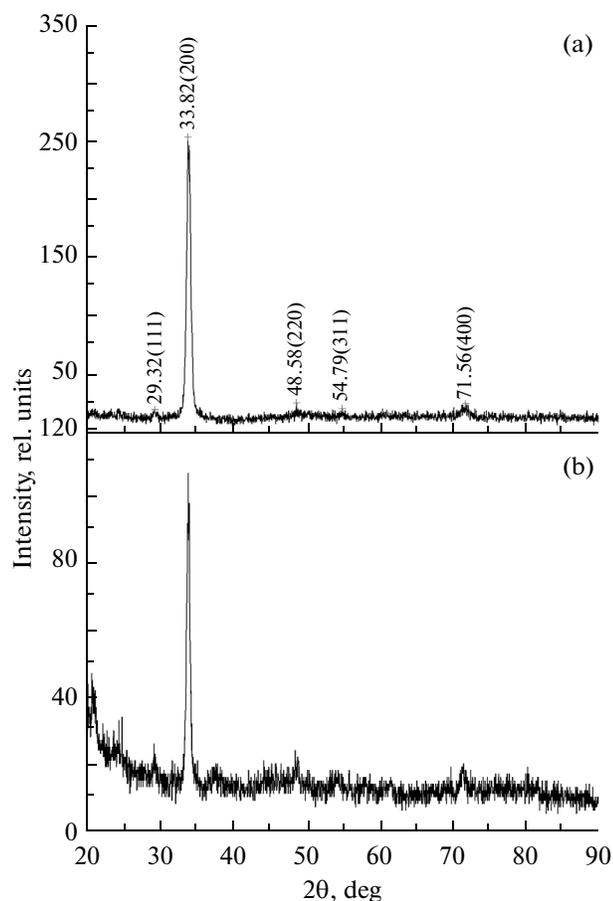
Fig. 1. XRD data on $Tm_xMn_{1-x}S$ samples with (a) $x = 0.1$ and (b) 0.15.

Fig. 2. Temperature dependences of magnetization for $Tm_xMn_{1-x}S$ solid solutions with $x = $ (*1*) 0, (*2*) 0.01, (*3*) 0.05, (*4*) 0.1, and (*5*) 0.15, measured in a magntic field of 10 kOe.

tures of 100–800 K in a magnetic field of 10 kOe. Resistivity was studied by means of four-probe dc compensation at temperatures of 80–1100 K.

RESULTS AND DISCUSSION

According to the XRD data (Fig. 1), the synthesized $Tm_xMn_{1-x}S$ samples had the NaCl-type cubic lattice characteristic of manganese monosulfide. Cation substitution while varying the composition from $x = 0.01$ to 0.15 raised unit cell parameter a from 0.5225 nm for α-MnS to 0.5306 nm for the $Tm_{0.15}Mn_{0.7}S$ composition, corresponding to an increase in the ionic radius of the substitute. No accompanying impurity phases were found in the synthesized samples. The crystal cleavage surface was studied via scanning electron microscopy and characteristic microphotographs of the thulium-doped crystals were obtained. Energy-dispersive X-ray spectroscopy (EDAX) data show that within instrument error, the thulium–manganese and thulium–sulfur ratios in the initial composition were consistent with those in the grown crystals.
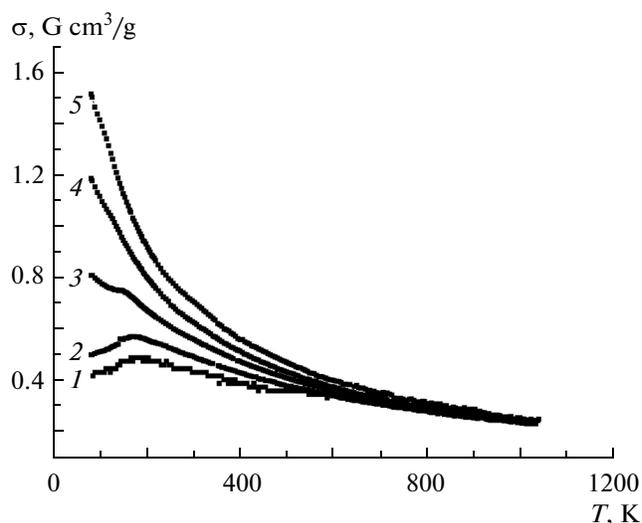
Figure 2 shows the temperature dependences of the magnetization of the $Tm_xMn_{1-x}S$ samples ($0 \leq x \leq 0.15$), measured in a magnetic field of 10 kOe. The temperature behavior of magnetization for the compositions with the low concentrations of substitute ($x \leq 0.01$) is qualitatively similar to the $\sigma(T)$ dependence for manganese monosulfide [12]. In the $\sigma(T)$ dependences of all compositions, we observe maxima indicative of the antiferromagnetic transition in the temperature range of 172 K at $x = 0.01$ to 130 K at $x = 0.15$, which becomes smaller as thulium concentration x rises. Using the temperature dependences of magnetic susceptibility, we established asymptotic paramagnetic temperature Θ_p, Curie–Weiss constant C, and effective magnetic moment μ_{eff}. The temperature dependence of inverse susceptibility $\chi^{-1}(T)$ in the high-temperature region is described by the Curie–Weiss law with paramagnetic temperature Θ, which has a negative value and grows from $\Theta_p = -478$ K at $x = 0.01$ to $\Theta_p = -69$ K at $x = 0.15$, indicating intensification of the ferromagnetic exchange due to the possible growth of superparamagnetic clusters with strong ferromagnetic interaction between the manganese ions nearest to thulium ions as a result of the kinetic exchange interaction. An increase in the degree of cation substitution is accompanied by variation in the effective magnetic moment in the range of (6–5.2) μ_B.

Our experiment showed that variation of the Tm concentration in the range of $x = 0.01$–0.15 also affected the kinetic properties of the synthesized $Tm_xMn_{1-x}S$ compounds in the temperature range of $80 \leq T \leq 900$ K. Figure 3 shows the temperature dependences of resistivity of the investigated $Tm_xMn_{1-x}S$

log ρ [Ω cm]

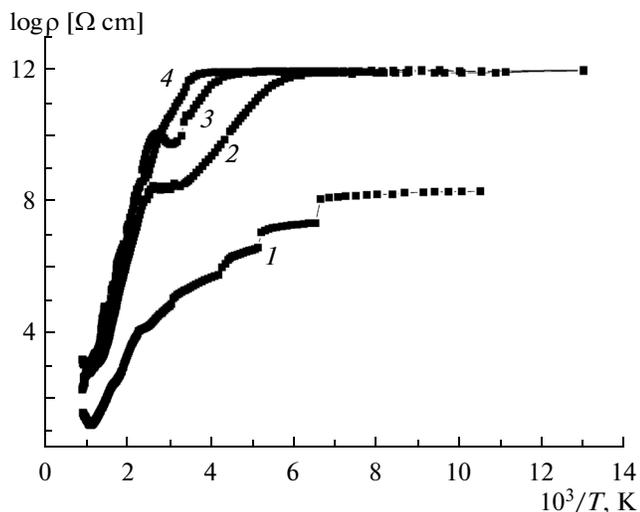**Fig. 3.** Temperature dependences of resistivity for $Tm_xMn_{1-x}S$ samples with $x = $ (*1*) 0.01, (*2*) 0.05, (*3*) 0.1, and (*4*) 0.15.

solid solutions. The behavior of the $\log\rho(10^3/T)$ curves is characteristic of substances with semiconductor conductivity analogous to manganese monosulfide. Using the slope of the linear part of $\log\rho(10^3/T)$, we determined the band gap of these compositions. It was found to change with temperature from 0.2 eV in the low-temperature region to 1.03 eV when $x = 0.05$. A similar situation was observed for the composition with $x = 0.1$, where the activation energy varied within $0.4-1.1$ eV. In the temperature range of $350-500$ K, the $\log\rho(10^3/T)$ curve of the samples with concentrations $x = 0.05$ and 0.01 contains anomalies characteristic of transitions from impurity to intrinsic conductivity. For $Tm_xMn_{1-x}S$ with $x = 0.01$ and 0.15, the $\log\rho(10^3/T)$ dependence shows no pronounced transition from impurity to intrinsic conductivity. In the temperature range of $150-240$ K, the $\log(10^3/T)$ dependence for all concentrations of the substitute contains jumps in conductivity that correlate with the temperatures of antiferromagnetic transition. In contrast to the resistivity of manganese monosulfide [12], all of the investigated samples were in the high-resistivity state even at room temperature. As the concentration of the RE element substituted in the MnS lattice rose, the resistivity grew from 200 kΩ at $x = 0.01$ to 280 GΩ when $x = 0.15$. The sharp rise in resistivity in the $Tm_xMn_{1-x}S$ solid solutions at low concentrations of the transition-metal ions substituted for Mn ions in the MnS lattice can be explained by the charge compensation effect; i.e., once incorporated into the MnS lattice, the transition-metal ions ensure donor conductivity, in contrast to the acceptor conductivity observed in the manganese monosulfide compound.

CONCLUSIONS

We synthesized new antiferromagnetic semiconductor compounds $Tm_xMn_{1-x}S$ ($0 \leq x \leq 0.15$) with a NaCl-type FCC lattice. We experimentally demonstrated that $Tm_xMn_{1-x}S$ solid solutions exhibit an interrelated combination of magnetic and conducting properties. It was found that the resistivity and magnetic moment of the investigated compounds grew when thulium ions with variable valence were substituted for manganese.

ACKNOWLEDGMENTS

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