Electrical resistance and impedance of manganese sulfides, substituted by lutetium

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Abstract. The effect of electron doping in $\text{Lu}_x\text{Mn}_{1-x}\text{S}$ and cationic vacancies in $\text{Mn}_{0.9}\text{S}$ manganese sulfide on the formation of phonon modes of vibration, the type of conductivity, and the impedance characteristics is studied. The IR spectra in the frequency range 450-7500 cm$^{-1}$, the I-V in the temperature range 300-500 K, and the impedance in the frequency range $10^2$-$10^6$ Hz were measured. The qualitative difference in the temperature behavior of the impedance, the activation character of the relaxation time, and the change in the activation energy of the impurity conductivity in $\text{Lu}_x\text{Mn}_{1-x}\text{S}$ at high temperatures are found.

1. Introduction

Semiconductors with electronic [1-3] and magnetic phase transitions [4-6], both in temperature and concentration, are promising materials for creating the element base of microelectronics. The transport of current carriers can be controlled both by action on the electron charge and the magnetic moment [7-12], in the presence of interaction between the electrons and the orbital magnetic moments [13-18]. In electrically inhomogeneous systems, the transport of current carriers in a magnetic field can be controlled on the basis of the Maxwell-Wagner effect [19-21] and the orbital ordering [22]. On the other hand, in systems with a random distribution of the electric potential and potential wells, it is possible to control the tunnel effects due to the external electric field [23-26] and the spin-phonon interaction [27-31].

To create electrically inhomogeneous states in manganese sulfide, the manganese ion is substituted by a trivalent lutetium ion. Nonstoichiometric substitution can lead to cationic defects [32]. To clarify the role of cationic defects, the $\text{Mn}_{0.9}\text{S}$ system is studied and its properties are compared with the $\text{Lu}_x\text{Mn}_{1-x}\text{S}$ solid solution. It is possible that substitution will lead to areas with increased conductivity and to the formation of a metallic bond. The presence of defective states is established from the IR spectra and electrical resistivity on direct and alternating current.

2. Materials and discussion of results

2.1. IR spectra

The IR spectrum was measured by the VERTEX80v Fouriertrans device with a resolution of 0.5 cm$^{-1}$ in the frequency range of 450-1200 cm$^{-1}$ and temperatures of 80-460 K. Figure 1a shows the IR absorption spectrum for $\text{Mn}_{0.9}\text{S}$, and figure 1b shows the IR spectrum of $\text{Lu}_x\text{Mn}_{1-x}\text{S}$ solid solutions for...
three concentrations. Below 700 cm$^{-1}$, we distinguish phonon bands at frequencies of 586-592 cm$^{-1}$ [33-34] for all three concentrations, and the intensity of the absorption bands decreases with increasing concentration. Weak absorption bands in the range of 515-527 cm$^{-1}$ and with increasing concentration, new absorption peaks appear at a frequency of 470 cm$^{-1}$. The phonon absorption frequencies are equal to the frequencies of 647 cm$^{-1}$, $\omega = 531$ cm$^{-1}$ in LaMnO$_3$ [35-37], which are associated with the oscillation modes of octahedra. It is possible that lutetium leads to deformation of octahedra containing manganese ions. At higher concentrations, the deformation of the octahedra decreases. In the Mn$_{0.9}$S sample, phonon modes of oscillations are absent in this frequency range.

In the frequency range 1000-1200 cm$^{-1}$, there is an absorption band that varies slightly with concentration and in Mn$_{0.9}$S it appears in the form of a kink. The existence of bands in the mid-IR range corresponds to localized electronic states and is observed in transition metal oxides and is considered as Jahn-Teller polarons, since vibronic coupling and the Jahn-Teller effect take place in the Mn-O octahedron. The polaron band was found in the La$_{0.9}$Sr$_{0.1}$MnO$_3$ manganite at an energy of ~ 0.15 eV [38, 39].

![Figure 1](image.png)

**Figure 1.** (a) IR absorption spectrum for Mn$_{0.9}$S and (b) Lu$_x$Mn$_{1-x}$S c x = 0.05 (1), 0.1 (2), 0.2 (3).

### 2.2 I-V and electrical resistance

The presence of electrically inhomogeneous states is determined from the I-V. The dependence of current on voltage in semiconductors can be described by Ohm's law, a power function, and an exponential function. In a strong electric field, the height of potential barriers can change, and the I-V is described by the Poole-Frenkel law [40]. In charge-ordered semiconductors, the conductivity is described in the model of currents bounded by a spatial charge [41]:

$$j = \frac{9}{8} \tau \mu \sigma_0 \frac{\nu^2}{L^3} S$$

where, $j$ is the current density, $\tau$ is the Maxwell relaxation time, $\sigma_0$ electrical conductivity in the volume of the material, $\mu$ is the carrier mobility, $U$ is the applied voltage, $L$ is the sample thickness, $S$ is the sample area.

Figure 2 shows the I-V for Lu$_x$Mn$_{1-x}$S. In a wide range of electric fields from 5 V to 200 V, the I-V in logarithmic coordinates lnI-lnU is described by a linear function lnI=A+lnnU with $n = 1.16$ at $T = 300$ K, $n = 1.3$ at $T = 450$ K for a concentration $x = 0.1$. With increasing concentration, the nonlinearity decreases and $n = 1.08$ at $T = 300$ K, $n = 1.16$ at $T = 450$ K. For concentrations is less than the percolation
concentration $X_c = 0.17$, the conductivity is described by the hopping type and approaches to the Mott law. If lutetium ions percolate through the lattice, the conductivity becomes ohmic.

![Figure 2](image2.png)

**Figure 2.** I-V of Lu$_x$Mn$_{1-x}$S solid solutions at temperatures $T = 300K$ (1), 340K (2), 380K (3), 420K (4), 450K (5), 500K (6) for $x = 0.1$ (a), $x = 0.2$ (b).

In a cationic non-stoichiometric sample with cation defects in Mn$_{0.9}$S, the I-V is a linear function with $n = 1.05$, the index does not depend on temperature (figure 3). The conductivity in the Mn$_{0.9}$S sample is ohmic. Manganese sulfides are Mott semiconductors with a charge gap formed by sulfur ions. Therefore, cationic vacancies do not significantly affect the conduction mechanism.

![Figure 3](image3.png)

**Figure 3.** I-V of Mn$_{0.9}$S solid solutions at temperatures $T = 300K$ (1), 340K (2), 380K (3), 420K (4), 460K (5).

In manganese sulfide, the band gap is 3 eV [42, 43]. Electron doping of $t_{2g}$ electronic states will lead to the formation of impurity states and, with increasing concentration, to the formation of an impurity subband [44, 46]. The energy interval between the valence band and the impurity state is found from the temperature dependence of the conductivity from the inverse temperature. For impurities semiconductors $R=R_0 \exp(\Delta E/kT)$ and the activation energy is determined from $\ln R=\ln R_0+\Delta E/kT$. Figure 4 shows the dependence of the electrical resistance on the inverse temperature.
With increasing concentration, the activation energy decreases from $\Delta E = 0.93$ eV for $x = 0.05$, $\Delta E = 0.86$ eV for $x = 0.1$ to $\Delta E = 0.7$ eV for $x = 0.2$. Perhaps this is due to the increasing of the impurity subband, and the increase in resistance above the percolation concentration is associated with a decrease in the mobility of current carriers. In the temperature range of 500-534 K, the activation energy changes. This can be caused by the pinning of lattice polarons or the formation of a charge density wave. Pinning of polarons is accompanied by lattice deformation. To verify this statement, it is necessary to carry out structural studies. Anomalies in the impedance spectrum can use as an indirect confirmation.

2.3 Impedance

Figure 5 shows the temperature dependences of the real part of the impedance and the normalized impedance $Z(T)/Z(T=90 \text{ K})$ for Lu$_x$Mn$_{1-x}$S with $x = 0.1$. In the vicinity of the temperature $T = 350 \text{ K}$, there is a maximum in the real part of the impedance, which disappears at high frequencies. This may be due to the formation of the charge ordering, which is accompanied by the deformation of the lattice. In the temperature range of 480-530 K, there is an electronic transition, which is accompanied by a maximum in the real part of the impedance and a maximum of the capacitance. The impedance abruptly decreases at the temperature of the magnetic phase transition as a result of the magnetoelastic interaction.

In a system with Mn$_{0.9}$S cationic defects, the temperature behavior of the impedance is qualitatively different (figure 6). When heated, the impedance decreases by 4-5 orders of magnitude above 200 K. A small maximum is observed at $T = 443 \text{ K}$, which does not depend on the temperature. The components of the impedance absolute magnitude have a maximum at this temperature. Apparently, this is due to local deformation near cationic vacancies [47, 48]. The change in the impedance from the temperature has an activation character $Z(T)=Z_0\exp(\Delta E/kT)$ with an activation energy $\Delta E = 0.11$-$0.13$ eV in the range of 250-500 K.
Figure 5. (a) – The real part of the Re(Z) impedance for Lu$_x$Mn$_{1-x}$S with $x = 0.1$ at the frequencies $\omega = 1$ kHz (1), 5 kHz (2), 10 kHz (3), 50 kHz (4), 100 kHz (5) and (b) – the normalized impedance $Z(T)/Z(T=90 \text{ K})$ at the frequencies $\omega = 1$ kHz (1), 5 kHz (2), 10 kHz (3), 50 kHz (4), 100 kHz (5), 300 kHz (6) for Lu$_x$Mn$_{1-x}$S with $x = 0.1$.

Figure 6. Logarithmic dependence of the impedance from the inverse temperature for Mn$_{0.9}$S. Temperature dependence of the imaginary (b) and real (c) parts of the impedance for Mn$_{0.9}$S at frequencies $\omega = 1$ kHz (1), 5 kHz (2), 10 kHz (3), 50 kHz (4), 100 kHz (5), 300 kHz (6).
The temperature behavior of the impedance components at room temperature and below is described in the Debye model:

\[
\text{Re } Z(\omega) = \frac{A}{1 + (\omega \tau_1)^2} \quad \text{Im } Z(\omega) = \frac{A \omega \tau_1}{1 + (\omega \tau_1)^2}
\]

where \(A\) is the constant parameters and \(\tau_1\) is the relaxation time the temperature dependence of which is described by the exponent \(\tau_1 = \tau_{10} \exp(\Delta E_1/kT)\) with activation energies of \(\Delta E_1 = 0.6\) eV.

3. Conclusion

In solid solutions of Lu\(_{x}\)Mn\(_{1-x}\)S, cationic vacancies are absent at the non-stoichiometric substitution. Phonon modes of octahedron oscillations, which are absent in Mn\(_{0.9}\)S, were found in the Lu\(_{x}\)Mn\(_{1-x}\)S compound. Electronic doping leads to a hopping type of conductivity and to a deviation of the current-voltage dependence from the Ohm's law. In manganese sulfide with cationic defects, Ohm's law is fulfilled. The impedance characteristics are qualitatively different. The active part of the impedance in Mn\(_{0.9}\)S increases at cooling below room temperature, passes through the maximum. The relaxation time of charged particles has an activation character. In Lu\(_{x}\)Mn\(_{1-x}\)S, the maximum resistance at the alternating current in the region of the electronic transition is found.

Acknowledgments

The reported study was funded by Grant of the President of the Russian Federation № MK-620.2021.1.2.

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