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The temperature dependence of the electrical characteristics of natural pyrite FeS$_2$ with the *p*-type conductivity in the temperature range of 295−635 K

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The results of the investigation of samples of natural hole−type pyrite FeS$_2$ are presented. The regularities of variations in their electrical properties with increasing temperature in the mode of uniform heating to 635 K are established. The results obtained are analyzed in terms of the dependence of the charge carriers diffusion intensity on temperature and material characteristics.

Keywords: pyrite, non−uniform doping distribution, temperature dependence of conductivity, thermal EMF, diffusion and drift currents.

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At present, the task of searching for low−cost semiconductor materials that might be used in creating thermal−to−electrical energy converters becomes more and more topical. Therefore, we concentrated our attention on sulfide materials that are, one the one hand, semiconductor materials with sufficiently high thermal−EMF coefficients α_T [1] and, one the other hand, often occur in nature and are relatively low−cost. One of the most widely spread sulfides is pyrite that is a binary sulfur−iron compound containing various impurities whose combinations characterize particular natural deposits of pyrite. Since sulfides, in particular FeS$_2$, are very common, their properties have been studied quite comprehensively. Previous studies devoted to pyrite are reviewed in [1]. For instance, it is known that there are two modifications of natural FeS$_2$ depending on specific deposits: *n*-conductive and *p*-conductive. Thermal−EMF coefficient α_T of these materials is inversely proportional to the free charge carrier (FCC) concentration. On the other hand, there are data contradicting the last statement and evidencing for an essential increase in pyrite α_T at high temperatures [1]. In the process of preliminary studying samples of natural hole−conductive pyrite by the hot probe method, we found out that coefficient α_T determined at different sample surface points ranges from +50 to +350 μV/K. This may be caused by the material inhomogeneity, e. g., variation in concentrations of acceptor doping atoms. Notice that investigation of non−uniformly doped semiconductor materials attracts at present a heightened attention due to, among other factors, observation of phenomena described in [2–4]. In recent times, investigation of such systems is being performed also for the purpose of enhancement of the efficiency of energy converters [5]. In this connection, the goal of this work was to study the natural pyrite electrophysical properties in the temperature range of 295 to 635 K, which could enable estimation of perspectiveness of using pyrite as a thermoelectric material at temperatures considerably lower than 540°C (813 K) above which thermal pyrite decomposition into iron sulfide (FeS) and elemental sulfur (S) is possible.

We considered samples of natural FeS$_2$ from two deposits of the Transbaikal Region; one of these deposits is characterized by the predominance of *n*-conductive pyrite, while at the other one *p*-conductive pyrite dominates. Preliminary investigations showed that the *p*-type pyrite is a mechanically strong material. The hot probe gets negatively charged at each sample point, coefficient α_T at 295 K varies from 50 to 350 μV/K depending on the location of the point where the hot probe is applied to the sample surface. Along with this, the 295 K specific resistance of the *p*-type samples is $\rho = 1.4 \cdot 10\,\Omega \cdot \mathrm{m}$, which compares favorably with the samples where the *n*-type conductivity prevails and specific resistance is an order of magnitude higher. At 295 K, coefficient α_T varies for them from −180 to +70 μV/K. Thus, such a pyrite needs to be preliminary sorted by the type of conductivity.

Thus, in this work we studied samples of the *p*-type pyrite for which preliminary investigation showed that they contain a single−type impurity non−uniformly distributed over the bulk.

In the course of the investigation, temperature dependences of voltage $U(T)$ fixed on the pyrite sample surface and of specific resistance $\rho(T)$ were measured in the interval of 295 to 635 K. The measurement setup layout is presented in Fig. 1. To ensure uniform heating of the sample, we used muffle furnace PM 8 (designated as *1* in Fig. 1) that contained a considerable mass of ceramics from which the chamber accommodating the material to be heated was fabricated. To prevent abrupt variations in temperature at the points of the sample−probe contact, a

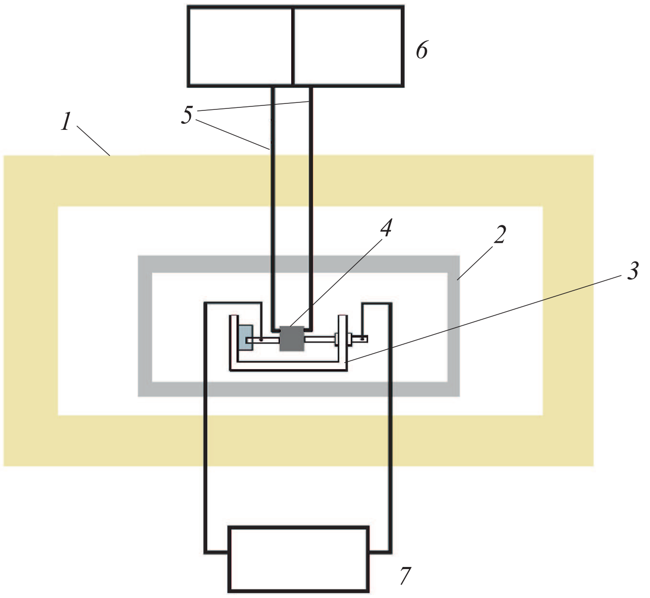

Figure 1. Design of the measurement cell used in studying electrophysical characteristics of pyrite samples, and its arrangement in the heating area of muffle furnace PM-8. *1* — muffle furnace PM-8, *2* — container, *3* — measurement cell, *4* — sample under study, *5* — thermocouples, *6* — multimeters DT 9205A, *7* — two−channel millivoltmeter AKTAKOM AMB 1084.

metal container *2* was put into the muffle furnace; this container played the role of a screen evening−out the effect of convection flows. The measurement cell *3* was located in the center of the container. The studied sample *4* was secured between the cell electrodes with a clamp bolt. The sample temperature at the points of contact with electrodes was controlled using thermocouples *5* whose signals were fed to two multimeters DT 9205A (*6* in Fig. 1). The signal from the sample was supplied to the two−channel millivoltmeter AKTAKOM AMB 1084 (*7* in Fig. 1).

Fig. 2 presents the temperature dependence of voltage $U(T)$ fixed on the sample. One can see that an increase in U is observed in the temperature range of 295 to 395 K, after which the voltage begins decreasing to zero (at 593 K), and then the voltage inverts its polarity and increases in modulus. Both the voltage increase and decrease stages possess sections where dU/dT changes its value. For instance, the section of linear voltage increase in the range of 295 to 345 K is replaced by that of a slower increase to the temperature of 395 K. As Fig. 3 shows, the specific resistance curve in the range of 295 to 395 K also has two sections (slow and rapid variation), which allows establishing the presence of correlation between the $U(T)$ and $\rho(T)$ behavior. This interrelation is observed also at higher temperatures. The presence of this interrelation evidences for the influence of the electronic system state transformation on the effect of voltage emergence on the facets of the uniformly heated sample. Since the specific resistance decrease with increasing temperature in a semiconductor material is accompanied by variations in the FCC concentration, it is possible to assume that the emergence of voltage on the sample facets is caused by the concentration gradient. In the case of natural pyrite considered in this study, the FCC concentration gradient may arise due to non−uniform distribution of the acceptor doping. Then the temperature increase in such a sample would cause a rapid change in the FCC concentration and, hence, a diffusion current promoting establishment of the internal electric field and drift current compensating the diffusion current:

$$eD_p \mathrm{grad} p = pe\mu E, \tag{1}$$

where e is the electron charge, D_p is the hole diffusion coefficient, μ is the FCC mobility, E is the internal electric field, p is the hole concentration. Taking into account the relationship between the diffusion coefficient and charge carrier mobility, obtain the U dependences on temperature, concentration and concentration gradient:

$$U = Ex = kT \mathrm{grad}(p)x/ep, \tag{2}$$

where x is the inter−probe distance, k is the Boltzmann constant.

Let us use relation (2) to analyze the temperature dependence of U presented in Fig. 2; we can see that the voltage increase on the sample in the temperature range of 295 to 345 K may be caused by the increase in temperature and concentration gradient. Then, as Fig. 3 shows, in the range of 345−395 K there is observed a decrease in the sample specific resistance, which evidences a growth of the hole concentration. Indeed, the estimates show that the specific resistance variation in the given range can no longer be explained only by a decrease in static FCC relaxation time due to enhancement of scattering from acoustic phonons.

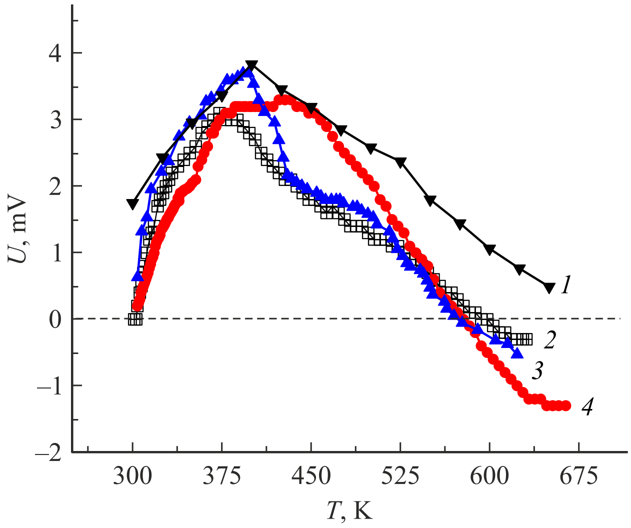

Figure 2. Temperature dependences of voltage fixed on different p-type pyrite samples (curves *2*−*4*). Curve *1* represents the $U(T, p)$ dependence calculated via relation (2) with the 25 K interval.

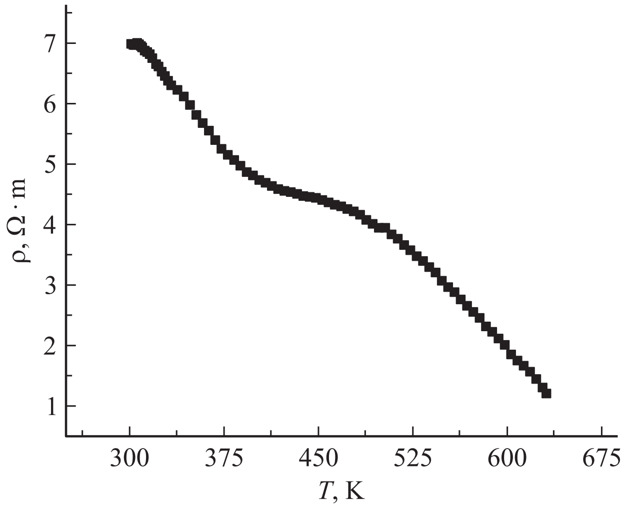

Figure 3. Temperature dependence of the *p*-type pyrite sample specific resistance whose dependence $U(T, p)$ is represented by curve *2* in Fig. 2.

Since the pyrite band gap is approximately 1 eV [1], the hole concentration increase in the range of 345−395 K is most probably caused by activation of carriers from doping atoms. Based on experimental data on the specific resistance behavior in this temperature range (see Fig. 3), the acceptor impurity activation energy $E_a = 0.116$ eV was obtained. Since, according to relation (2), the voltage on the sample is inversely proportional to the FCC concentration, the growth of p makes voltage to attain saturation in the range of 345−395 K (Fig. 2). Thus, relation (2) provides qualitative description of the observed regularities of the $U(T, p)$ behavior. This conclusion is confirmed also by calculations of the theoretical dependence described by (2) which is represented in Fig. 2 by curve *1*. In calculation, it was taken into account that the charge carrier mobility decreases with increasing temperature because of enhancement of their scattering from the lattice acoustic vibrations, while the FCC concentration gradient increases in the region of impurity conductivity proportionally to factor $e^{-(E_a/kT)}$.

As Fig. 3 shows for temperatures above 395 K, the specific resistance decreases with increasing temperature with the rates that are different in the ranges of 425 to 520 K and 520 to 635 K. The specific resistance behavior at the temperatures of 425 to 520 K may be explained by termination of the impurity ionization, while in the range of 520 to 635 K this behavior is explained by the transition to intrinsic conductivity. Based on the curve $\rho(T)$ slope in the temperature range of 520−635 K, we determined the carrier activation energy that appeared to be 1.05 eV; this agrees well with the literature data on the pyrite band gap ranging from 0.77 to 1.2 eV [1]. The transition to intrinsic conductivity and emergence of free electrons more mobile than holes in the sample bulk containing the electric field caused by non−uniform doping distribution results in that electrons get accumulated in the region with a lower concentration of the acceptor doping. This is just why the sign inversion of voltage fixed on the sample takes place at a temperature exceeding 600 K. Notice that the transition to intrinsic conductivity at temperatures above 525 K is favorable for using pyrite as a mid−temperature thermoelectric material. In addition, once the conditions for emergence of thermal EMF are fulfilled, namely, an abrupt temperature change occurs on the natural pyrite sample, accounting for the direction of internal field caused by the impurity concentration gradient may be used to increase its thermoelectric efficiency.

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Conflict of interests

The authors declare that they have no conflict of interests.

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