05.2;07.2;09.1

The temperature dependences of the electrical characteristics of nature pyrite *n* in the range 295−635 K

© N.P. Stepanov, G.I. Grabko

Transbaikal State University, Chita, Russia
E-mail: np-stepanov@mail.ru

Received December 12, 2022
Revised April 16, 2023
Accepted April 20, 2023

The results of the investigation of the hole nature pyrite sample *n* are presented. The regularities of change of 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 diffusion intensity of charge carriers from temperature and materials characteristics

Keywords: pyrite, not uniform doping distribution, temperature dependence of conductivity, thermal EMF, diffusion and drift currents.

DOI: 10.61011/TPL.2023.06.56379.19459

The physical properties of pyrite (FeS_2), which is one of the most abundant sulfides, need to be studied in order to evaluate its potential as a thermoelectric material. Seebeck coefficient α of pyrite may be as high as 200 μV/K at 297 K and grows with temperature [1]. Its electric conductivity also increases markedly (by 1-2 orders of magnitude) with temperature in the region of impurity conductivity [2]. Since both *n*- and *p*-type pyrite is found in nature, it has the potential to be used as a base material for a thermoelectric element. It is also known that impurities are often distributed nonuniformly in natural pyrite [3]. The examination of such materials assumes importance in light of the current heightened interest in the study of phenomena observed in nonuniformly doped semiconductors and their application in electrical engineering [4,5]. However, several technological problems, which are concerned primarily with separation of pyrrhotite from pyrite, need to be solved in order to prepare this mineral for application in semiconductor engineering. One should also find a way to separate *n*-type pyrite from *p*-type one. The temperature region within which impurity conductivity remains dominant and the temperature of the onset of a transition to intrinsic conductivity have been determined in our earlier studies. It turned out that this temperature for pyrite, which has a band gap width of approximately 1 eV, is close to 525 K [6]. Thus, pyrite is a viable candidate medium-temperature thermoelectric material.

One of the aims of the present study is to examine the temperature dependence of resistivity of natural *n*-type pyrite, which was identified by the sign of Seebeck coefficient α using the hot probe method. It was found that the value of Seebeck coefficient α varied both from one sample to another and within a single sample. The temperature dependence of resistivity was studied for all samples. The experimental procedure and technique were detailed in [6].

Temperature dependences $\rho(T)$ of resistivity of three studied natural *n*-type pyrite samples are presented in Fig. 1. These dependences reveal the semiconductor nature of samples. It can be seen that their resistivity increases sharply in the 420−450 K temperature range. It follows from Fig. 1 that the resistivity dependences have certain features in the temperature interval from 420 to 525 K. In pyrite, this interval corresponds to temperatures at which the ionization of impurities nears completion and the transition to intrinsic conductivity starts. Thus, relaxation process, which are attributable to carrier scattering off lattice vibrations, are likely to affect the observed resistivity variation.

However, the nature of this variation calls attention to itself. Estimates do indeed indicate that if the variation of free carrier density is excluded and the increase in effective mass of carriers within a narrow temperature interval of 420−450 K, where the resistivity jump is observed, is neglected, the reduction in static relaxation time due to a more intense scattering of nondegenerate carriers off acoustical lattice vibrations, which is proportional to T^{-2}, may provide a roughly 15% enhancement of resistivity, whereas the enhancement magnitude averaged over five studied samples is 38%. Since the resistivity enhancement is observed within the temperature region of proposed thermoelectric applications of pyrite, it is of current interest to determine the causes of the above discrepancy.

The resistivity jump is observed at a high temperature; therefore, carrier scattering off optical phonons may also produce a certain contribution to this phenomenon. In view of this, a study aimed at determining the frequencies and energies of optical phonons in pyrite was undertaken. Figure 2 shows the spectral dependences of the reflection coefficient of two pyrite samples measured using an IFS-113V (Bruker) infrared Fourier spectrometer at a temperature of $T = 295$ K. The angle of radiation incidence onto a sample was 7°.

It can be seen that the reflection coefficient spectra of both samples feature a series of peaks with the same positions. The reflection spectrum structure in Fig. 2 may be interpreted as a band of residual rays formed due to the excitation of optical lattice vibrations of this mineral [7]. Such bands are typical of substances with a fraction of ionic bonding and several atoms in a lattice cell [8]. Conspicuous is the fact that the energy of the spectral range containing the optical phonon excitation band varies from 37 to 54 meV and corresponds to the values of energy kT of thermal vibrations falling within the interval from 420 to 626 K. Thus, the abrupt increase in resistivity of the studied samples, which is observed in Fig. 1, occurs within this temperature interval. Therefore, the increase in resistivity of pyrite observed in the 420–450 K temperature range may be attributed to a more intense carrier scattering off optical phonons. It is known that carriers interact most efficiently with longitudinal optical phonons, which have their scattering parameter $r = -1/2$ and relaxation time varying in accordance with the following expression: $1/\tau \sim T\varepsilon^{-1/2}$. If the variation of carrier energy ε within a small temperature interval of 420–450 K is neglected, a more intense scattering off optical phonons may provide a maximum resistivity enhancement of 7%. Therefore, according to the Matthiessen rule, the joint contribution of scattering off acoustical and optical phonons provides an approximately 22% resistivity enhancement, which is 1.7 times smaller than the observed value. Thus, a certain additional mechanism specific to the studied material and contributing to the resistivity enhancement is likely to be present in this case. A resistivity variation similar to the one observed in Fig. 1 was indeed revealed in the examination of natural pyrrhotite $Fe_{1-x}S_x$ [4]. It is known that magnetization also increases rapidly in pyrrhotite within approximately the same temperature region where resistivity features are observed. The magnetization enhancement

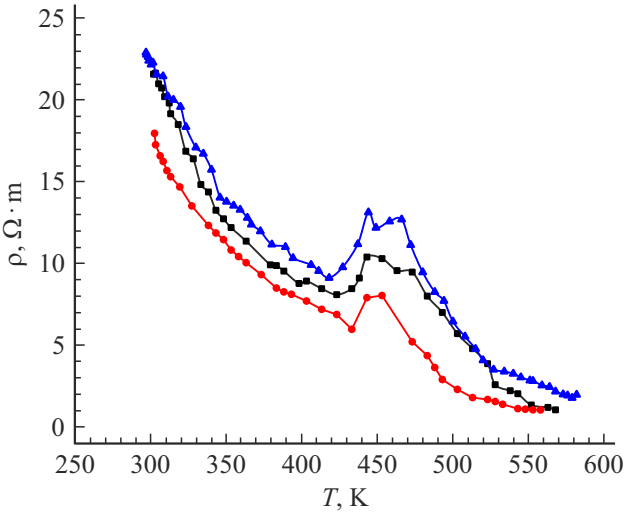

Figure 1. Temperature dependences of resistivity of three studied natural *n*-type pyrite samples.

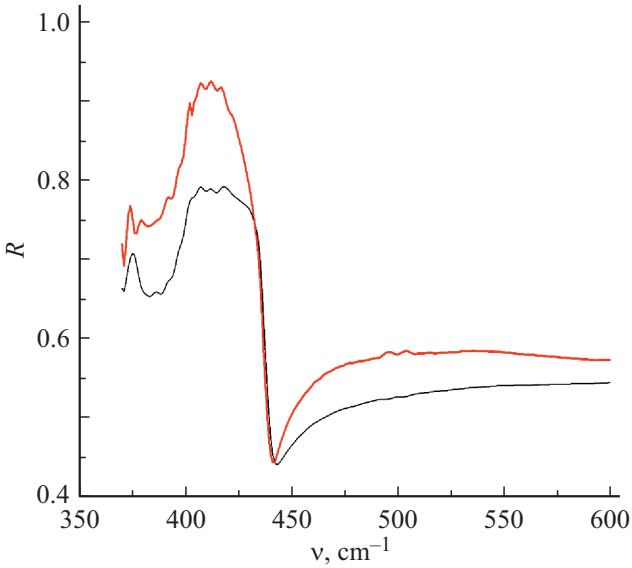

Figure 2. Spectra of the reflection coefficient of two natural *n*-type pyrite samples at a temperature of 295 K.

underlies the transition from an antiferromagnetic state to a ferrimagnetic one (the so-called γ-transformation [9]). Thus, natural *n*- and *p*-type pyrite was milled with subsequent separation in a 5 kOe magnetic field. It was found that natural *p*-type pyrite available to us, which was examined in [6], does not contain magnetically active inclusions. At the same time, approximately 12 wt.% of magnetically active matter were extracted in the present study from *n*-type pyrite milled into fragments no greater than 500 μm in size. This is indicative of the necessity of magnetic separation and removal of pyrrhotite from pyrite. The data reported in [4] do indeed suggest that the presence of a considerable amount of pyrrhotite may induce an enhancement of resistivity of a sample in the region of temperatures preceding the onset of intrinsic conductivity of pyrite, thus reducing the thermoelectric power value.

We note in conclusion that pyrite is a semiconductor with its free carrier density varying within a wide range as a function of temperature and the type and amount of doping impurities. The estimates reported in [7] indicate that a high free carrier density, which increases with temperature, may be observed in a pyrite sample containing a large amount of impurity of a certain type. The energies of plasmons and longitudinal optical phonons may converge in this case, thus intensifying the plasmon-phonon interaction that produces a potential contribution to carrier scattering within a certain temperature interval.

Funding

This study was supported financially by grant No. 22-22-20055 (https://rscf.ru/project/22-22-20055/) from the Russian Science Foundation and by the Government of Zabaykalsky Krai.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] N.P. Stepanov, S.A. Nemov, I.V. Sveshnikov, G.I. Grabko, A.N. Vlasov, A.V. Leskov, A.A. Kalashnikov, L.E. Stepanova, Fiz. Tekh. Poluprovodn., **55** (9), 826 (2021) (in Russian). DOI: 10.21883/FTP.2021.09.51303.9667
[2] A.I. Ginzburg, *Metody mineralogicheskikh issledovanii* (Nedra, M., 1985) (in Russian).
[3] R.G. Shui, *Poluprovodnikovye rudnye materialy* (Nedra, L., 1979) (in Russian).
[4] Yu.V. Ulashkevich, V.V. Kaminskiy, M.V. Romanova, N.V. Sharenkova, Semiconductors, **52** (2), 172 (2018). DOI: 10.1134/S1063782618020227.
[5] V.V. Kaminskii, S.M. Solov'ev, N.M. Sudak, M.I. Zaldastanishvili, Tech. Phys. Lett., **46** (1), 47 (2020). DOI: 10.1134/S1063785020010071.
[6] N.P. Stepanov, G.I. Grabko, Tech. Phys. Lett., **48** (12), 22 (2022). DOI: 10.21883/TPL.2022.12.54940.19347.
[7] N.P. Stepanov, V.M. Tupikov, V.M. Lapushkov, Fiz. Zemli, No. 1, 79 (1994) (in Russian).
[8] R.K. Willardson, A.C. Beer, *Semiconductors and Semimetals* (Academic Press, 1967).
[9] V.V. Onufrienok, Fiz. Tekh. Poluprovodn., **23** (10), 3198 (1981) (in Russian).

Translated by D.Safin