ISSN 0020-1685, Inorganic Materials, 2018, Vol. 54, No. 8, pp. 757–759. © Pleiades Publishing, Ltd., 2018.
Original Russian Text © N.I. Il'inykh, L.E. Kovalev, 2018, published in Neorganicheskie Materialy, 2018, Vol. 54, No. 8.

# Effect of Background Fe Impurities on the IR Absorption and Dielectric Response of High-Resistivity ZnSe Single Crystals

**N. I. Il'inykh[a] and L. E. Kovalev[b, *]**

[a] *Ural Technical Institute of Communication Systems and Information Sciences, Siberian State University of Telecommunications and Information Sciences (Yekaterinburg Branch), ul. Repina 15, Yekaterinburg, 620109 Russia*

[b] *Uman National University of Horticulture, Institutska vul. 1, Uman, Cherkassy oblast, 20305 Ukraine*

**e-mail: leokova60@yahoo.com*

Received November 3, 2017; in final form, January 16, 2018

**Abstract**—High-resistivity zinc selenide crystals containing background impurities have been studied by IR spectroscopy and dielectric spectroscopy. Their IR absorption spectra contain a band attributable to the presence of background Fe impurities in the material. The dielectric characteristics of the ZnSe crystals lead us to conclude that, because of a nonuniform distribution of background impurities, they have the form of matrices containing inclusions.

*Keywords:* zinc selenide, transmission spectrum, dielectric permittivity

**DOI:** 10.1134/S0020168518080083

## INTRODUCTION

Zinc selenide is a promising material for the production of semiconductor electronic devices. At present, it is widely used as a material for the fabrication of optical components; high-power, high-current Schottky diodes; and X-ray and neutrino detectors. All this makes the study of the properties of ZnSe a topical issue. Korotkov et al. [1] and Belenchuk et al. [2] investigated single-crystal ZnSe samples which exhibited photocurrent surges and slow relaxation after preliminary optical excitation. The effect was shown to be due to background Fe impurities. Fe impurities can be detected in IR absorption spectra, and nonuniform distributions of background impurities and native defects would be expected to influence the dielectric characteristics of the material. Vaksman et al. [3] studied optical absorption in Fe-doped ZnSe single crystals. Chugai et al. [4, 5] investigated the dielectric properties of nominally undoped and chromium-doped zinc selenide crystals.

The purpose of this work was to study high-resistivity single-crystal ZnSe samples by IR spectroscopy and dielectric spectroscopy.

## THEORETICAL ANALYSIS

Using electron paramagnetic resonance (EPR) before and after heat treatment in liquid zinc and liquid bismuth, nominally undoped ZnSe single crystals with background impurities were shown to contain a number of defects which could change vibrational modes in their local environment [6]. Defects locally disturb the vibrational spectrum and can produce localized vibrational modes. Background impurities and defects in ZnSe crystals have a strong effect on the optical absorption in the material. Inclusions and inhomogeneities in the bulk of a ZnSe crystal, which are characterized by a variety of impurity states, cause large optical losses due to light scattering.

The dielectric characteristics of high-resistivity ZnSe crystals with background impurities in the frequency range $10^{-2}$ to $10^9$ Hz cannot be described in terms of Debye's classical dispersion theory, which is applicable in the optical frequency range with some approximations.

The low-frequency dielectric permittivity of a material is determined by several physical mechanisms, which have a polarizing effect. Because of this, experimental data are typically inconsistent with Debye's classical model.

Jonscher's empirical law is more universally applicable. The essence of this law is that all the range of the frequency dependence of dielectric characteristics can be divided into regions where the dielectric permittivity can be described by power law functions with different exponents [7]. In the maximum dielectric loss region ($\omega_{max}$), the dielectric permittivity can be represented as follows:

$$\varepsilon'(\omega) \sim \varepsilon(0) - a\omega^m; \quad \varepsilon''(\omega) \sim \omega^m \ (\omega \ll \omega_{max}); \tag{1}$$

$$\varepsilon(\omega) \sim \frac{1}{1 + i\omega/\omega_{max}}; \quad \omega \approx \omega_{max}, \tag{2}$$

$$\varepsilon(\omega) \sim (i\omega)^{n-1}; \quad \omega \gg \omega_{max}, \tag{3}$$

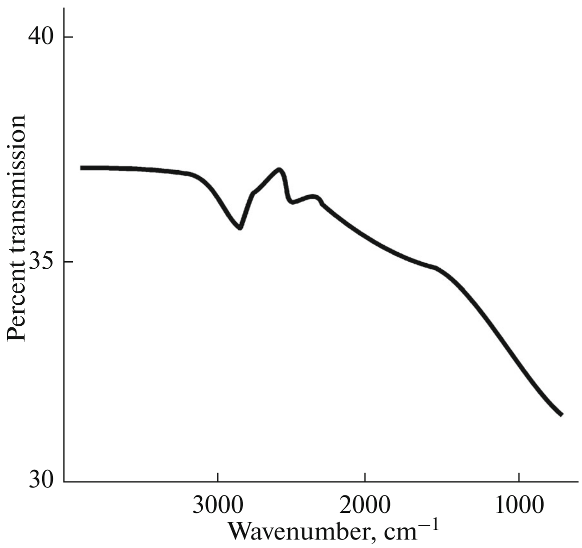


**Fig. 1.** IR transmission spectrum of high-resistivity ZnSe.

where the parameter $a$ is frequency-independent, $\omega_{max}$ is the peak dielectric loss frequency, and the exponents meet the inequalities $0 \le m, n \le 1$.

In the case of dielectric systems with a high electrical conductivity at low frequencies, we have

$$\varepsilon''(\omega) \sim \omega^{-p}, \quad 0 \le p \le 1. \tag{4}$$

## EXPERIMENTAL

ZnSe samples for assessing impurity-related absorption were prepared by cleaving bulk single crystals with the sphalerite structure along (110) planes and had the form of plane-parallel plates ranging in thickness from 0.2 to 0.5 mm. The transmission spectrum of ZnSe was measured on a Specord 75 spectrophotometer in the range 4000 to 400 cm$^{-1}$ at a temperature of 294 K.

The dielectric response of any material can be represented as the time dependence of a depolarization current, which causes the polarization field $E_0$ to disappear:

$$i(t) = \frac{dP}{dt} = \varepsilon_0 E_0 \varphi(t), \tag{5}$$

where $P(t)$ is the time-dependent polarization of the sample, $\varepsilon_0$ is the dielectric permittivity of vacuum, and $\varphi(t)$ is the dielectric response function.

On the other hand, the dielectric response can be described by the frequency dependence of the complex dielectric permittivity $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$, which is the Fourier transform of the dielectric response $\varphi(t)$.

This fact underlies the working principle of the setup used in our measurements, which offers the possibility of assessing dielectric characteristics of various materials at frequencies from $10^{-2}$ to $10^6$ Hz and temperatures from 130 to 450 K. In the frequency range $10^5$ to $10^9$ Hz, the dielectric characteristics of high-resistivity ZnSe containing background impurities were studied using an experimental setup whose working principle is based on the use of the lumped capacitance method. This method relies on the fact that the capacitance of a waveguide changes when a sample to be studied is introduced into one of its sections [8].

## RESULTS AND DISCUSSION

Figure 1 shows a typical transmission spectrum of nominally undoped ZnSe crystals, which exhibited a photocurrent surge, in the range 4000 to 700 cm$^{-1}$. The spectrum demonstrates two absorption bands: at 2860 cm$^{-1}$ (0.355 eV) and 2500 cm$^{-1}$ (0.310 eV).

Vaksman et al. [3] attributed the absorption band at 2860 cm$^{-1}$ (0.355 eV) to intracenter transitions of the $Fe^{2+}$ ion. The origin of the absorption band at 2500 cm$^{-1}$ (0.310 eV) has not been identified.

Thus, the IR absorption spectra of the ZnSe crystals were found to contain a band at 2860 cm$^{-1}$ (0.355 eV), which was tentatively attributed to the presence of Fe impurities.

Figures 2 and 3 show the frequency dependences of the real and imaginary parts of the dielectric permittivity for the ZnSe crystals at different temperatures. To analyze these data, we used parameterization [7] based on formulas (1)–(4).

The ZnSe crystals containing background impurities were observed to have a weak low-frequency dielectric loss peak (Fig. 3). The temperature range from 290 to 440 K turned out to be of most interest for analysis. The frequency dependence of the imaginary part of the dielectric permittivity for the ZnSe crystals can be divided into three distinct portions differing in slope. In the low-frequency region, where the dielectric loss is dominated by the contribution of conduction electrons, the frequency dependence of permittivity can be described by the power law relation $\varepsilon''(\omega) \sim \omega^{-p}$, with an exponent $p = 0.71$. Proceeding from Jonscher's versatile law, we determined the exponent in the region of the dielectric loss peak at $\omega > \omega_{max}$: $1 - n = 0.96$. Using approximation in the region of the loss peak at $\omega < \omega_{max}$, we obtained $m = 0.01$.

Thus, at low frequencies and high temperatures, the dielectric response of the ZnSe crystals studied here is contributed primarily by their dc conductivity. Their dielectric properties are characterized by one loss peak, with a very small exponent $m = 0.01$ and a very high value $1 - n = 0.96$. Such behavior of the frequency dependence of $\varepsilon''(\omega)$, with a highly asymmetric dielectric loss peak, is typical of inhomogeneous materials with potential barriers [7]. If there is a relatively high concentration of free current carriers, a major contribution to the dielectric loss is made by deep localized states near a potential barrier.

## REFERENCES


1. Korotkov, V.A., Bruk, L.I., Simashkevich, A.V., Gorea, O.S., Kovalev, L.E., and Malikova, L.V., Deep centers influence on photoresponse characteristics in high-resistivity ZnSe, *Mater. Res. Soc. Symp. Proc.,* 1997, vol. 442, pp. 579–584.
2. Belenchuk, A.V., Ilyinykh, N.I., and Kovalev, L.E., Secondary ion mass spectroscopy of zinc selenide crystals with photoconductivity spectral memory, *Russ. Phys. J.,* 2017, vol. 59, no. 10, pp. 1718–1720.
3. Vaksman, Yu.F., Nitsuk, Yu.A., Yatsun, V.V., Nasibov, A.S., and Shapkin, P.V., Optical absorption and diffusion of iron in ZnSe single crystals, *Semiconductors,* 2010, vol. 44, no. 4, pp. 444–447.
4. Chugai, O.N. et al., Dielectric properties of ZnSe crystals grown from melt, *Phys. Solid State,* 2010, vol. 52, no. 12, pp. 2467–2471.
5. Chugai, O.N. et al., Effect of dopant Cr ions on the dielectric properties of melt-grown ZnSe crystals, *Phys. Solid State,* 2013, vol. 55, no. 1, pp. 60–63.
6. Korotkov, V.A., Kovalev, L.E., Bruk, L.I., Gorea, O.S., Ketrush, P.I., and Malikova, L.V., Effect of thermal annealing in Bi and Zn melts on local centers in ZnSe, *Mater. Res. Soc. Symp. Proc.,* 1998, vol. 487, pp. 505–510.
7. Jonscher, A.K., Dielectric relaxation in solids, *J. Phys. D: Appl. Phys.,* 1999, vol. 32, no. 14, pp. R57–R70.
8. Feldman, Yu., Gusev, Yu.A., and Vasilyeva, M.A., *Dielectric Relaxation Phenomena in Complex Systems: Tutorial,* Kazan: Kazan Univ., 2012, p. 134.


*Translated by O. Tsarev*