

## KRAMERS-KRONIG ANALYSIS OF $Ni_{1-x}Zn_xFe_2O_4$ FERRITES INFARED DIFFUSE REFLECTANCE SPECTRA

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The results of the analysis of infrared spectra  $Ni_{1-x}Zn_xFe_2O_4$  ferrite are presented [1] by Kramers - Kronig. The spectra of  $n$ ,  $k$ ,  $\varepsilon_i$ ,  $\varepsilon_r$ ,  $\text{Im}(\varepsilon^{-1})$  are calculated. As is known, the process involves the addition of ions Zn to the structure of zinc-nickel ferrite in the form  $(Zn_x^{2+}Fe_{1-x}^{3+})[Ni_{1-x}^{2+}Fe_{1+x}^{3+}]O_4$ , where there is change in the zinc in the substrate to the coherent change of Fe in A- and B-sublattices and Ni in B. On the sublattice, the ion junctions are derived from the A sublattice of the subgroup of Ni octahedral voids, thereby forming the  $FeO_6$  complex. Precisely, this process is accompanied by changes in charge and spins distributions, and, consequently, with superfluous and double bonded interconnections of cation nickel and glue. It is shown that the observed spectra of spectra are reflected by the ferrite correlation with the  $Ni^{2+}$ ,  $Zn^{2+}$ ,  $Fe^{2+}$  and  $Fe^{3+}$  concentrations in the different concentrations.

**Keywords:** Kramers-Kronig analysis, IR spectra, ferrites

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The features of the infrared diffuse reflectance spectra of  $Ni_{1-x}Zn_xFe_2O_4$  ferrites with different concentrations of Zn [1] in the range from  $4000\text{ cm}^{-1}$  to  $50\text{ cm}^{-1}$  were interpreted by analyzing the results of studies of these spectra by the Kramers-Kronig (KK) procedure. The spectral dependences  $n(\omega)$ ,  $k(\omega)$ ,  $\varepsilon_i(\omega)$ ,  $\varepsilon_r(\omega)$  and loss function  $\text{Im}(\varepsilon(\omega))^{-1}$  are established. The KK method has long been used to analyze the reflection spectra to obtain various optical parameters of materials [2-15]. This can be due to it being easier to develop and can be applied to analyze a wide variety of materials (organic to inorganic, solid to liquid, and single crystal, polycrystalline, and amorphous) without reference to specific models. However, the application of the KK method was hindered by its complexity of the integration.

Many algorithms have been proposed for the Kramers-Kronig (KK) analysis [16]. However, none can be applied to any reflection spectrum without giving rise to unphysical effects. Furthermore, they do not make possible determination of the values of the optical constants; only the shape of the optical constants spectra is determined, more or less precisely. In this paper an algorithm for KK analysis is presented in which the disadvantages described above are removed as far as possible [17]. This algorithm can be applied for any reflectivity ( $R$ ) spectrum measured in the visible or ultraviolet, in the energy range  $(\omega, \omega_0)$ . As additional data, the curve for the absorption coefficient ( $\alpha$ ) in the range  $(0, \omega)$  is required. KK analysis is based on the use of the following formula [18]:

$$\theta(\omega_0) = \frac{\omega_0}{\pi} \int_0^{\infty} \frac{\ln R(\omega) - \ln R(\omega_0)}{\omega^2 - \omega_0^2} d\omega \quad (1)$$

where  $\theta$  denotes the phase shift of the electromagnetic wave on reflection. The KK integral (1) requires a knowledge of  $R$  throughout the entire energy range, not only in the measuring energy range  $(\omega, \omega_0)$ . Thus, the necessity for  $R$ -extrapolations in both the low-energy range  $(0, \omega)$  and the high-energy range  $(\omega_0, \infty)$  arises. Obviously, the artificial  $R$ -extrapolation never gives the same values of  $\theta$  as the experimental  $R$ -curve. Thus, there is an extrapolation error in the calculated optical constants.

The method of extrapolation error determination presented previously [19] tends towards overestimation of the error.

The infrared reflectance spectroscopy is a main tool for optical investigations in the IR spectral range. The optical parameters of a system under investigation, the dielectric function  $\varepsilon(\omega)$  or the optical conductivity  $\sigma(\omega)$  which is directly related with the dielectric function as  $\varepsilon(\omega) = 1 + i4\pi\sigma(\omega)/\omega$  are determined from the reflectivity spectrum  $R(\omega)$  making use of the KK relations. The KK analysis, however, requires for extrapolations of the experimental data to the low- and high-frequency limits, which usually essentially reduces an accuracy of the analysis. We present an algorithm of the Kramers-Kronig analysis based on an anchor-window technique. The high-frequency asymptote of the reflectivity spectrum is determined by a minimization of differences between the KK-deduced optical conductivity  $\sigma_{KK}(\omega)$  and the known  $\sigma(\omega)$  values, measured a priori in a small anchor-window.

Following results with KK relations are expressed figure 1.

The analysis of IR spectra of investigated compositions of  $Ni_{1-x}Zn_xFe_2O_4$  ferrites in  $4000\text{ cm}^{-1}$  -  $500\text{ cm}^{-1}$  range shows that the information about IR spectra of  $ZnO$ ,  $NiO$  and  $Fe_2O_3$  components is necessary for interpretation of spectral peculiarities (see fig.1).

The complex reflectance spectrum is mathematically decomposed into two separate spectra - extinction coefficient and refractive index spectrum. These are also called K and N spectra. The real ( $n$  = refractive index) and imaginary ( $k$  = extinction) parts of the complex index of refraction are calculated from the reflectance spectrum using the following formulas:

$$\begin{aligned} n(\omega) &= \frac{1 - R(\omega)}{1 + R(\omega) - 2\sqrt{R(\omega)} \cos(\theta(\omega))} \\ k(\omega) &= \frac{2\sqrt{R(\omega)} \sin(\theta(\omega))}{1 + R(\omega) - 2\sqrt{R(\omega)} \cos(\theta(\omega))} \end{aligned} \quad (2)$$

where  $R$  is the reflectance,  $n$  – wavenumber,  $\theta$  – phase shift angle of the sample.

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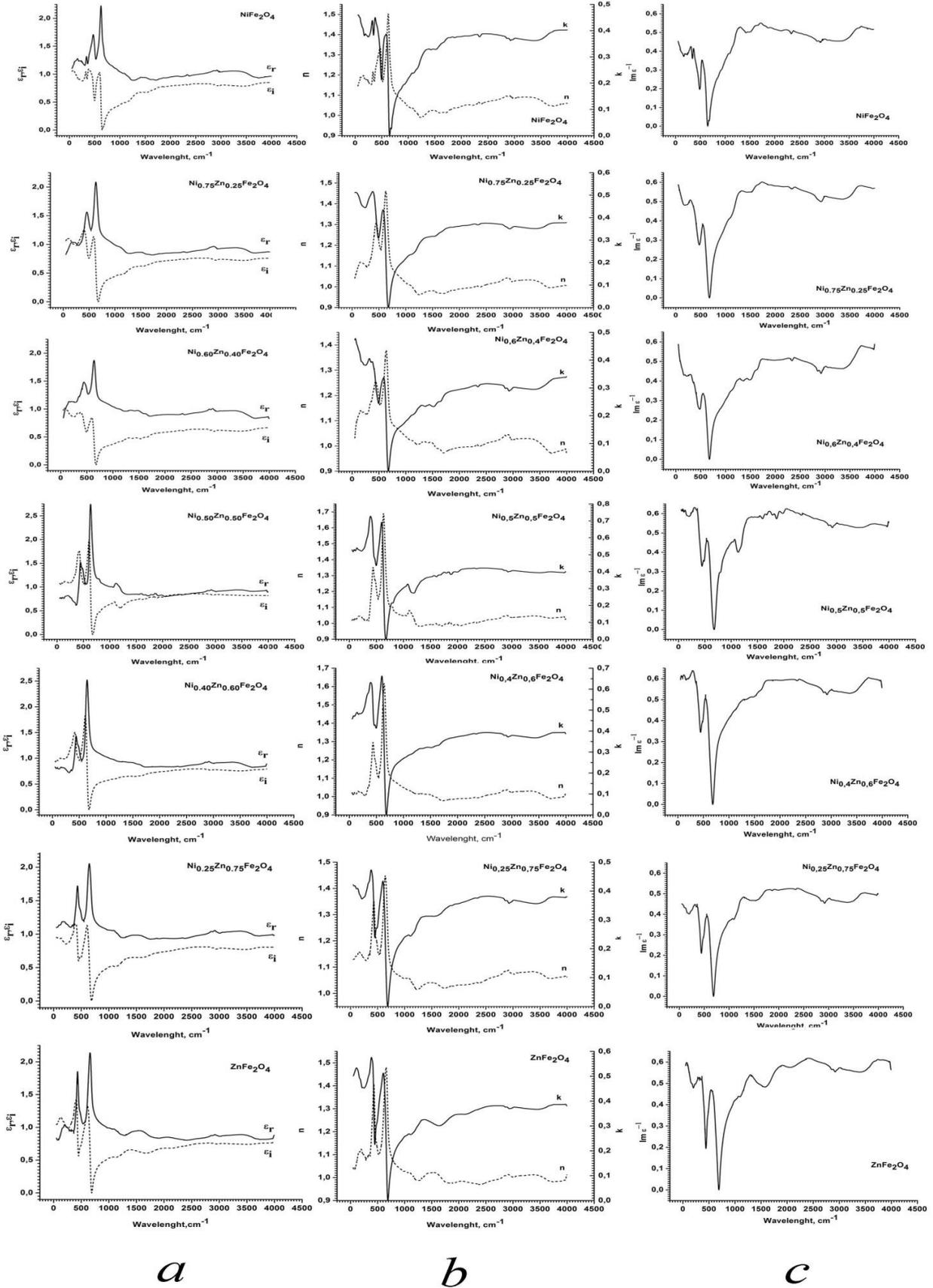


Fig.1 Dependence of  $\epsilon_r$ ,  $\epsilon_i$ ,  $n$ ,  $k$  and  $\text{Im}(\epsilon^{-1})$  of  $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$  ferrites in different concentrations.

Extrapolation to zero frequency is easy to produce if we suggest that the reflection  $R$  approaches a value that is usually known and remains constant. It is assumed that in the extrapolation region there is no sharp structure characteristic for interband transitions. The reflection should be quite high at frequencies below the frequency of plasma oscillations and rapidly decrease at frequencies greater than the plasma frequency. In this case, the change in reflection is given by the expression:

$$R(\omega) = c\omega^{-4}$$

For a given wavenumber, the phase shift is calculated using the equation (3):

$$\begin{aligned} \varepsilon_r(\omega) &= (n^2 - k^2)_{\omega_0} = 1 + \frac{2}{\pi} \int_0^{\infty} \frac{\omega \varepsilon_i(\omega)}{\omega^2 - \omega_0^2} d\omega \\ \varepsilon_i(\omega) &= (2nk)_{\omega_0} = -\frac{2\omega_0}{\pi} \int_0^{\infty} \frac{\varepsilon_r(\omega)}{\omega^2 - \omega_0^2} d\omega \end{aligned} \quad (3)$$

As it is known, the incorporation of Zn ions into the structure of the nickel-zinc ferrite is recorded in the form of  $(Zn_x^{2+}Fe_{1-x}^{3+})[Ni_{1-x}^{2+}Fe_{1+x}^{3+}]O_4$ , that is, a change in the zinc content in the A-sublattice leads to a consistent change in the Fe content in the A and B-sublattices and Ni in the B-sublattice, the iron ions being displaced from the A-sublattice to the octahedral sites of the B-sublattice released from Ni, that is, forming  $FeO_6$ . Naturally, such a process is accompanied by changes in charge and spin distributions and, consequently, super- and double exchange interactions involving nickel and iron cations. It is shown that the observed changes in the reflection spectra of these ferrites are connected with the redistribution of  $Ni^{2+}$ ,  $Zn^{2+}$ ,  $Fe^{2+}$  and  $Fe^{3+}$  ions concentration in different compounds.

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