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Studying of dielectric spectra of $YCu_{0.15}Mn_{0.85}O_3$ solid solution with the use of complex conductivity

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This work presents the results of studying the electrophysical properties of the $YCu_{0.15}Mn_{0.85}O_3$ solid solution in the range of temperatures of $T = 26$–$400\,^{\circ}C$ and frequency range of $f = 10^2$–10^5 Hz. A model description of the revealed dispersion of dielectric parameters in the material is made. The nonclassical modified Havriliak–Negami model written for complex electrical conductivity was used as an approximation model. It is shown that the application of this model almost exactly describes the frequency behavior of the dielectric constant $\varepsilon'/\varepsilon_0(f)$, the dielectric loss tangent $\mathrm{tg}\delta(f)$ as well as the real and imaginary parts of complex conductivity $\gamma'(f)$ and $\gamma''(f)$. The results of this work are an important step in identifying the opportunities and understanding the applications of this model.

Keywords: Multiferroics; yttrium manganite; relaxation; Havriliak–Negami model; complex conductivity.

1. Introduction

Dielectric spectroscopy methods, which are widely used in modern materials science and various fields of physics, chemistry, biology, etc. for studying the electrophysical properties of objects and the features of their real structure, have been successfully used for more than 40 years. Their development is currently a rather important and urgent task. In the field of physical materials science, substances are very popular in which several types of orderings manifest themselves simultaneously. Such objects are called multiferroics. In view of the presence in them of interactions between various subsystems, mainly ferroelectric (FE) and magnetic,[1,2] they are given special attention due to their great potential for application in modern technological industries.

Yttrium manganite ($YMnO_3$) is a low-temperature multiferroic with an antiferromagnetic transition at $T_N \approx 80$ K, which has a high Curie temperature of $T_C \approx 900$ K.[3,4] Interest in this object, in particular, is because the minimum total energies of its hexagonal and orthorhombic structural states are very close.[5] Thus, at room temperature, it can be obtained in the form of both a rhombohedron and a perovskite.

Nonisovalent substitution in solid solutions based on $YMnO_3$ (as well as other manganites in general) has an interesting feature associated with a change in the valency of manganese in the "chain" $Mn^{(4+)}O_2$ (873 K) $\rightarrow$ $Mn_2^{(3+)}O_3$ (1173 K) $\rightarrow$ $Mn_3^{(2+)+(3+)}O_4$ (1573 K). Moreover, the temperatures of its transitions can be even lower in multi-element compositions. Thus, low doping with copper leads to the fact that in $YCu_xMn_{1-x}O_3$ solid solutions prepared by traditional ceramic technology, the hexagonal phase is stabilized in concentrations up to 15%, and $YCu_{0.15}Mn_{0.85}O_3$ is formed practically without impurities.[6] This indicates a partial transition of $Mn^{3+} \rightarrow Mn^{4+}$ in the *B*-positions. In addition, when studying the grain structure of $YCu_{0.15}Mn_{0.85}O_3$, traces of a liquid phase of presumably eutectic origin were found. All these suggest that in this object the conductivity increases quite sharply, which, as is known, complicates the study of dielectric properties, in the temperature–frequency behavior of which, as a rule, a strong relaxation is observed.

Describing the most dispersive dielectric spectra, the Havriliak–Negami model (1) (Refs. 7–9) is traditionally used, where, using the parameters α and β, varying within

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[0; 1], it can be obtained the laws of Debye ($\alpha = 0$, $\beta = 1$), Cole–Cole ($0 \le \alpha \le 1$, $\beta = 1$) and Davidson–Cole ($\alpha = 0$, $0 \le \beta \le 1$),

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{(1+(i\omega\tau)^{1-\alpha})^\beta}, \quad (1)$$

where $\varepsilon^* = \varepsilon' - i\varepsilon''$ is the combined complex dielectric permittivity; ω is the angular frequency (rad/s); ε_0 denotes the values of ε at $\omega \to 0$ [low-frequency (LF) region]; ε_∞ denotes the values of ε at $\omega \to \infty$ [high-frequency (HF) region]; and τ is the most probable relaxation time, *s*.

Moreover, for materials with high conductivity, this model provides for the singular term, which significantly helps to improve the percentage of convergence of strongly relaxing dielectric spectra.[7,10–14]

Some more complex models, for example, the Dissado–Hill distribution (2),[7,15–17] describe the experimentally observed dispersion in dielectrics quite accurately,

$$\varepsilon^* = \frac{\varepsilon_\infty + \Delta\varepsilon(1-n+m)_2F_1\left(1-n,1-m,2-n,\frac{1}{1+j\omega\tau}\right)}{\Gamma(2-n)\Gamma(m)(1+j\omega\tau)^{1-n}}, \quad (2)$$

where ${}_2F_1$ is the Gaussian hypergeometric function.

Despite the fact that these models are successfully used in dielectric spectroscopy, very often there exist significant discrepancies between the model and experiment in the HF and LF regions, which was also discovered by us in the course of investigations of the dielectric properties of promising lead-free materials based on potassium niobate.[18] For the description, a new model was proposed based on (1), which makes it possible to describe the dispersion of the complex conductivity using the following relation[19]:

$$\gamma^* = \gamma_\infty + \frac{\gamma_s - \gamma_\infty}{(1+(i\omega\tau)^{1-\alpha})^{1-\alpha}} + \varepsilon''_\infty\omega\varepsilon_0 + i\varepsilon'_\infty\omega\varepsilon_0, \quad (3)$$

where $\gamma^* = \gamma' + i\gamma''$ is the combined complex electrical conductivity; $\varepsilon''_\infty\omega\varepsilon_0$ is the singular term that shows the reach-through conductivity contribution in γ'; ε''_∞ denotes the values of ε'' at $\omega \to \infty$; $\varepsilon'_\infty\omega\varepsilon_0$ is an additional term; and ε'_∞ denotes the values of ε' at $\omega \to \infty$.

As studies have shown in this model, the parameter α is no longer "adjustable", as it was in model (1), but is a parameter of the temperature–frequency distribution of dielectric losses,[19]

$$\alpha = \frac{kT}{E_a}\ln Q_\infty, \quad (4)$$

where Q_∞ is the quality factor at $\omega \to \infty$.

Applying model (3), it became possible to accurately describe complex spectra, the behavior of which has a strong relaxation character.

In this work, we present the results of a study of the dielectric spectra of ceramics of the $YCu_{0.15}Mn_{0.85}O_3$ solid solution by using formula (3).

2. Research Objects and Methods

In the synthesis of ceramics of the $YCu_{0.15}Mn_{0.85}O_3$ solid solution, simple oxides Y_2O_3, CuO and Mn_2O_3 were used with a quality not lower than "analytical grade". The stoichiometric mixture was stirred in ethylene for 1 h, after which it was briquetted into discs 5 mm in diameter. The stage of synthesis was carried out stepwise at temperatures of $T_1 = 850\,°C$ ($t_1 = 3$ h) and $T_2 = 1160\,°C$ ($t_2 = 2$ h).

Temperature dependences ($T = 26$–400 K) of the relative permittivity, $\varepsilon'/\varepsilon_0(T)$, and the dielectric loss tangent, $\mathrm{tg}\delta(T)$, in the frequency range of $f = 10^2$–10^5 Hz were obtained using a measuring stand based on the LCR-meter HIOKI 35–50 using Method no. GSSSD ME 184–2011. For measurements, auromal 38 paste (DODUCO GmbH) was applied to the ceramic surface. The relative permittivity ($\varepsilon/\varepsilon_0$) was determined from the relation $C = \varepsilon\varepsilon_0 S/h$, where C is the structure capacitance, h is the thickness of the ferroelectric layer, S is the electrode area and $\varepsilon_0 = 8.854 \times 10^{-12}$ F/m is the electric constant.

The relaxation processes in dielectric spectra were approximated by formula (3) using the developed computer program.[20]

3. Results and Discussion

Detailed results of studying X-ray structural analysis and microstructure are presented in Refs. 6 and 21. Figure 1 shows the dependences of $\varepsilon'/\varepsilon_0(T)$ and $\mathrm{tg}\delta(T)$ for the $YCu_{0.15}Mn_{0.85}O_3$ ceramics in the temperature range of $T = 26$–$400\,°C$ and the frequency range of $f = 10^2$–10^5 Hz. The values are plotted in a logarithmic scale. At room temperature, the ceramics were characterized by low values of the relative permittivity (40–80) and a high value of the dielectric loss tangent (up to 5), which is a consequence of the high-through electrical conductivity of ceramics [$\gamma_s \sim 10^{-6}$ $(\Omega\cdot\mathrm{m})^{-1}$], which gives a

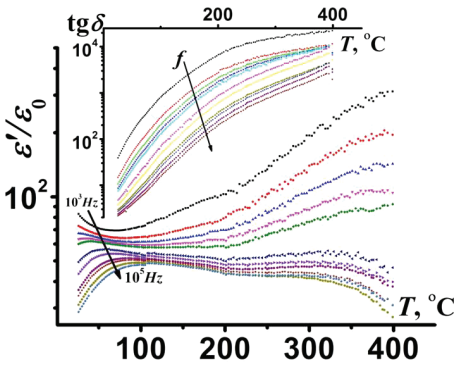


Fig. 1. Temperature–frequency dependences of $\varepsilon'/\varepsilon_0(T)$ and $\mathrm{tg}\delta(T)$ of $YCu_{0.15}Mn_{0.85}O_3$.

direct contribution of $\gamma_s/(\varepsilon_0\omega)$ to tgδ.[7] On the $\varepsilon'/\varepsilon_0(T)$ curves, in all cases, as the temperature increased at the range of T = 26–120 °C, maxima were formed at T_m, the position of which, with an increase in f from 10^3 Hz to 10^5 Hz, shifted to the high-temperature region: from 40°C to 102°C in visible region.

In turn, anomalies on the dependences of tg$\delta(T)$ in this region were identified rather weakly and mainly at the highest frequencies in the form of "humps" or inflection points, which is due to the previously noted contribution to the dielectric response of the through electrical conductivity of objects, which increases with increasing temperature (see inset of Fig. 1). The $T_m(f)$ dependence in the analyzed frequency range for $YCu_{0.15}Mn_{0.85}O_3$ ceramics was described by the Arrhenius relation

$$f = f_0 e^{\frac{E_{act}}{kT_m}}, \tag{5}$$

where f_0 is the frequency of attempts to overcome the potential barrier E_{act} and k is the Boltzmann constant.

The high electrical conductivity of ceramics, which, as has been repeatedly noted in the literature, can be different between the grain volume and the grain boundary, leads to the accumulation of charges at such interfaces, which differ in dielectric parameters.[7] The rather complex heterophase and heterogeneity of ceramics are shown in Refs. 6 and 21. In addition, given that this solid solution is in the ferroelectric phase (space group $P6_3cm$), the screening of spontaneous polarization by free charges also plays an important role. All these on the whole contribute to the manifestation of the effects of interlayer polarization (Maxwell–Wagner polarization) and the accompanying dielectric relaxation, the consequence of which we fix on the dependences of $\varepsilon'/\varepsilon_0(T)$ and tg$\delta(T)$.

Dielectric loss is the dissipation of energy due to the movement of charges in an alternating electromagnetic field when polarization changes direction. The nature of the dielectric response of materials can be understood by studying the change in dielectric loss with frequency. Therefore, to begin with, the frequency dependences of $\varepsilon'/\varepsilon_0(f)$ and tg$\delta(f)$ were plotted at room temperature. Further processing was carried out using formula (3). For this, the experimental data were used to calculate the values of the real and imaginary parts of the complex conductivity, as well as the figure of merit at high frequencies (Q_∞). Using the software[20] and formula (4), the value of the parameter of the temperature–frequency distribution of dielectric losses (α) was calculated and the approximation of the frequency dependences of $\varepsilon'/\varepsilon_0(f)$, tg$\delta(f)$, $\gamma'(f)$ and $\gamma''(f)$ was done. During the approximation, the value of the activation energy E_a was found, corresponding to model (3), and the corresponding relaxation time (τ) was calculated.

Figures 2 shows the dependences of $\varepsilon'/\varepsilon_0(f)$, tg$\delta(f)$ and $\gamma'(f)$ of the experimental data at room temperature. The form of the dependences of $\varepsilon'/\varepsilon_0(f)$ and tg$\delta(f)$ indicates

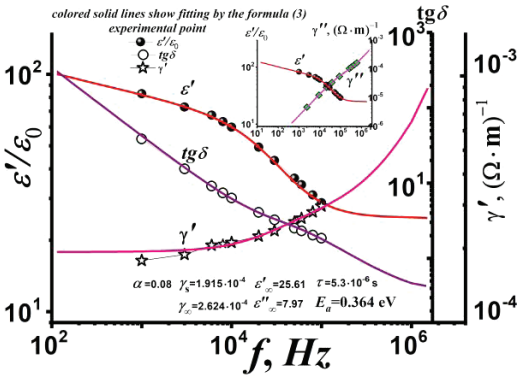


Fig. 2. The frequency dependences of $\varepsilon'/\varepsilon_0(f)$, tg$\delta(f)$ and $\gamma'(f)$ at room temperature. The frequency dependences of $\varepsilon'/\varepsilon_0(f)$ and $\gamma'(f)$ are in the inset. Solid lines are the result of approximation by formula (3).

the occurrence of dielectric relaxation in the object, with a large contribution of the through electrical conductivity. As noted earlier, this kind of dependence is rather difficult to describe with the classical models of Debye, Cole–Cole and Davidson–Cole.

Therefore, an attempt was made to use a nonstandard representation of the Havriliak–Negami model through complex electrical conductivity. Earlier, in the course of our research on the modification of the Havriliak–Negami model to the form (3), it was found that the activation energy has some discrepancies with the values from the classical laws. For example, in the PZT sample, relaxor-type anomalies did not have distinct maxima[19]; therefore, E_a was calculated according to the Arrhenius laws $\tau(T)$ and $\gamma(T)$, and not according to the Fogel–Fulcher law (5). This led to the fact that the obtained energies were presented in the form of "effective" values.[19] However, the calculations and experiments carried out later made it possible to reduce the discrepancies to a minimum. It was shown that the Arrhenius law could also relate the values of conductivity in the HF and LF regions:

$$\gamma_\infty^* = \gamma_0^* e^{\alpha\frac{E_a}{kT}}, \tag{6}$$

where γ_∞* is the complex conductivity at $\omega \to \infty$; and γ_0* is the complex conductivity at $\omega \to 0$ ($\gamma_0^* = \gamma_s^*$), which made it possible to make some corrections at calculating the activation energy.

In the case of considering the $YCu_{0.15}Mn_{0.85}O_3$ solid solution, as shown above, the relaxor anomaly has pronounced maxima, which made it possible to apply the Fogel–Fulcher law (5) and calculate the activation energy E_a = 0.360 eV.[6] Further, taking into account the relations (4) and (6), the experimental spectra were described using the presented model (3) and the corresponding values of the activation energy and relaxation time were calculated (Fig. 2), which turned out to be in agreement with our earlier data.[6] This is a big step in the

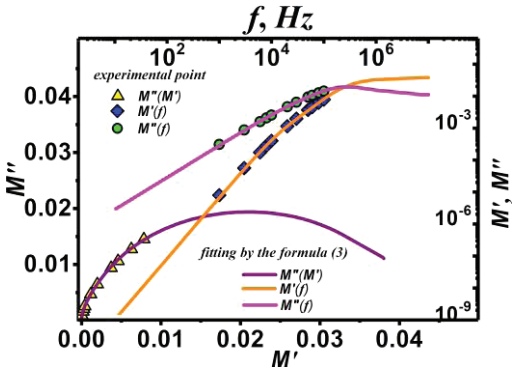


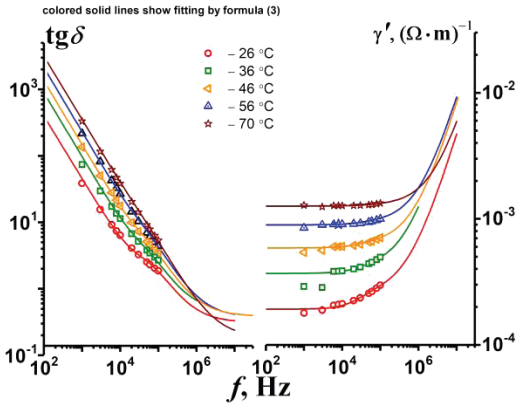
Fig. 3. A Cole–Cole diagram with the frequency dependences of $M'(f)$, $M''(f)$ and $M''(M')$. Solid lines are the result of approximation by formula (3).

application of the model (3), taking into account the fact that it shows almost complete convergence with the experimental points. Thus, we can conclude that the model for describing dielectric spectra, written for complex conductivity, can be used in the case of highly conductive ceramics, for example, such as solid solutions of the $YCu_xMn_{1-x}O_3$ multiferroic ceramics.

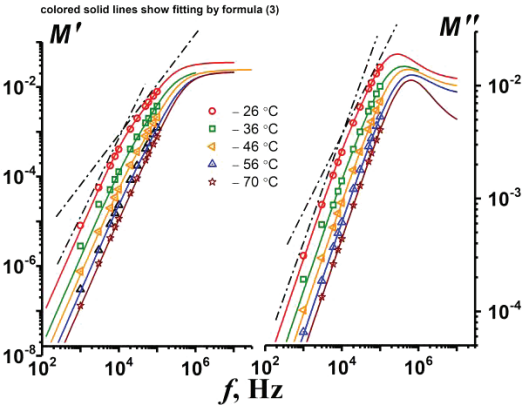
A suitable tool for studying various relaxation mechanisms is the Cole–Cole diagram.[22] In the ideal Debye case, it is a semicircular arc centered on the abscissa axis. Since most of the systems under study are imperfect, due to the presence in them of various local inhomogeneities, conductivity, the effect of interlayer polarization, etc., the center of the Cole–Cole diagram is shifted below the axis. When studying the frequency behavior, for convenience, we constructed a Cole–Cole diagram in the modules $M'(f)$, $M''(f)$ and $M''(M')$ as shown in the following equation (Fig. 3):

$$M' = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2}, \qquad M'' = \frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2} \tag{7}$$

In view of the small number of points, the description using the model (3) is rather predictive in nature. It is clearly seen that the center of the theoretical circle lies well below the abscissa axis. This fact is another evidence of the efficiency of this model of complex electrical conductivity.



(a)



(b)

Fig. 4. Dependences of (a) $tg\delta(f)$ and $\gamma'(f)$ and (b) $M'(f)$ and $M''(f)$ of $YCu_{0.15}Mn_{0.85}O_3$ at different temperatures.

For verification, frequency dependences were constructed and processed by the method described above at other temperatures with obtaining similar results, which are shown in Fig. 4.

The summary data of the used experimental values and obtained values in the process of approximation of the key quantities are shown in Table 1. It can be seen that with an

Table 1. Main parameters which were obtained from the experimental data and calculated using formulas (3) and (4).

T (°C)	α	$\tau \cdot 10^{-6}$ (s)	$\gamma_s \cdot 10^{-4}$ ($\Omega \cdot m$)$^{-1}$	$\gamma_\infty \cdot 10^{-4}$ ($\Omega \cdot m$)$^{-1}$	ε'_∞	ε''_∞	E_a (eV)
26	0.08	5.30	1.915	2.624	25.61	7.97	0.364
36	0.07	5.10	3.687	4.182	33.57	14.89	0.335
46	0.07	5.00	5.865	6.381	35.69	13.85	0.349
56	0.07	4.80	8.933	9.357	40.14	14.89	0.383
70	0.14	4.50	12.62	12.90	44.64	8.31	0.359

increase in temperature, the approximation had an ever-greater convergence. In addition, it should be noted that the previously shown anomaly in the dependences of tgδ, which disappears with increasing temperature and frequency, is also described by the proposed theory. From these data, we can conclude that model (3) can become an additional tool in the study of dielectric spectra and can be applied especially in cases where the classical models give a strong discrepancy.

4. Conclusions

In the $YCu_{0.15}Mn_{0.85}O_3$ solid solution, the measured dielectric spectra were studied using a new model based on the Havriliak–Negami model and recorded for complex conductivity. It has been shown that it is capable of describing spectra with a strong relaxor behavior due, among other things, to the presence of high conductivity. As a result of the approximation, the values of activation energy and the corresponding relaxation time were obtained, which are consistent with those data obtained by us earlier. It should be noted that, despite the small number of investigated frequencies, it was possible to fully approximate all experimental data. In this case, the convergence was achieved in the process of describing simultaneously not only $\varepsilon'/\varepsilon_0(f)$, tg$\delta(f)$, $M'(f)$, $M''(f)$ and $M''(M')$, but also $\gamma'(f)$ and $\gamma''(f)$, which indicates the reliability of the obtained results. These results are important for further exploration of the applicability of this model.

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