Examination of dielectric dispersion of complex oxides on the basis of bismuth-containing titanates

M.S. Shashkov¹, O.V. Malyshkina¹, E.V. Barabanova¹, M.S. Korolyova², I.V. Pily²

¹Tver State University, Tver, Russia
²Komi Institute of Chemistry of Ural branch of Russian Academy of Sciences, Syktyvkar, Russia

e-mail: Olga.Malyshkina@mail.ru

Abstract. In the present work the samples of complex oxide compounds on the basis of bismuth titanates with chalcolamprite structure type and layered perovskite doped with Cr, Fe and Co were studied at room temperature by the method of dielectric spectroscopy in the frequency range of 30 to 10⁶ Hz.

1. Introduction
One trend of modern materials science is the replacement of lead-containing materials with lead-free equivalents. In the present work we study the samples of bismuth-containing compounds which are of interest with respect to utilizing their dielectric properties. Complex bismuth titanates with layered perovskite structure are ferroelectric with high Curie temperature. They are used for the production of radio capacitors, piezoelectric transmitters, filters, sonar devices, etc.

Complex oxides of bismuth titanate with a structure of layered perovskite and pyrochlore doped by Cr, Fe and Cu in accordance with the stoichiometric formulas Bi₁,6Ti₂Cr₀,16O₆,6, Bi₁,55Ti₁,97Cu₀,78O₇ and Bi₄Ti₂Fe₂O₁₁,5 were studied. The dielectric properties were measured in the frequency range from 30 Hz to 10⁶ Hz. The low value of the voltage applied to the samples allowed to exclude the nonlinear polarization processes.

2. Sample preparation
The polycrystalline samples of iron-containing bismuth titanate with designated composition were prepared by the procedure of solid phase synthesis in air using Bi₂O₃ (99.99%), TiO₂ (99.999%) and Fe₂O₃ (99.9%) Cr₂O₃ (99.9%), CuO (99.9%) in stoichiometric ratios. Before sintering, the starting oxides were mixed in an agate mortar for 30 minutes, pressed into pellets and put into a corundum crucible. The pellets were first sintered for 6 h at 650°C (below 825°C which is the melting point of Bi₂O₃ and is within the temperature range of its phase transition). Then several sintering processes with intermediate grinding and pelleting were carried out at 950 °C (5 h), 1050 °C (5 h) and 1100 °C (5 h) for Cr-doped pyrochlore. The samples were cooled down to room temperature with the furnace. The evaporation of Bi₂O₃ was not detected neither by the thermogravimetric measurements nor by the elemental analysis of the samples.

3. Theory
Analysis and presentation of the experimental data were performed using the fractal-power universal law for the dielectric response. According to this law the response is presented by a power function,
whereby $\varepsilon'(f)$, $\varepsilon''(f)$, as well as the $\sigma'(f)$ and $\sigma''(f)$ are described as a power function of the applied field frequency $[1]$. In this case the responses due to either dipole or mobile charge carriers are separated. It is to be noted that there are two independent processes of the dielectric response. The dipole relaxation is characterized by a maximum in the $\varepsilon''(f)$ dependence, while there is no maximum in the response due to mobile charge carriers.

For the case of dipole relaxation, the determination of relaxation parameters was carried out by an analysis of the experimental data, which consists of the following:

1) determination of the frequency shift corresponding to the maximum of $\varepsilon''(f)$,
2) analysis of the $\varepsilon''(T)$ dependence in Arrhenius coordinates.

In the case of conductivity relaxation such an analysis is not possible, so an empirical calculation method $[2]$ was applied. The idea behind this method is to introduce a value $\beta^* = 1/\varepsilon^*$, where the expressions for $\beta'$ and $\beta''$ have the form

$$
\beta' = \frac{\varepsilon'}{(\varepsilon')^2 + (\varepsilon')^2}, \\
\beta'' = \frac{\varepsilon}{(\varepsilon')^2 + (\varepsilon')^2}.
$$

Whereas there is no maximum in the curves $\varepsilon''(f)$, it may be observed in the $\beta''(f)$ curves. In view of the relaxational type of the conductivity the analysis of its dispersion was performed making use of the relation $\delta(f) = \tan^{-1}(\varepsilon''/\varepsilon')$, which is the inverse of the dielectric loss tangent $(\tan\delta = \phi^{-1}(f))$.

4. Results and Discussion

The frequency dependence of the complex dielectric characteristics for $\text{Bi}_{1.6}\text{Ti}_{2}\text{Cr}_{0.16}\text{O}_{6.6}$, $\text{Bi}_{1.55}\text{Ti}_{1.97}\text{Cu}_{0.78}\text{O}_{7}$ and $\text{Bi}_{4}\text{Ti}_{2}\text{Fe}_{1}\text{O}_{11.5}$ ceramics was obtained. The results for the dielectric permittivity, conductivity, dielectric module and dielectric loss tangent are shown in Figures 1 and 2, respectively.

There is no difference in the form of dielectric spectra of investigated materials (Fig.1, a). The only disparity is in the magnitudes of the real parts of permittivity $\varepsilon'(f)$. The absence of a maximum in the frequency dependence of the imaginary parts of permittivity $\varepsilon''(f)$, which characterizes the dielectric loss, allows to assume that the nature of the response is due to the presence of mobile charge carriers. In this case the use of the empirical calculation method of finding the relaxation times becomes validated.

Frequency behaviour of the dielectric module is illustrated in Figure 1(b). The presence of the maxima on the graphs of $\beta''(\omega)$ allows to determine the relaxation times as the reciprocal of the corresponding cyclic frequencies for all the samples under study (Table 1).

![Figure 1](image-url)
The frequency dependence of the conductivity is of the power function type (Figure 2 (a)), \( \sigma \sim \omega^s \). Most of the authors interpreted this dependence in terms of the hopping conductivity model in the two-site approximation, independently of the investigated frequency range. It is obvious that with decreasing frequency, when the characteristic the hopping length is comparable to the average distance between the centers of localization, a transition to the hopping of the charge carriers by multi-site clusters (the multiplet conductivity) should be observed. In the theoretical works [2] it was shown that this transition does not lead to the anomalous changes in the behavior of \( \sigma(f) \). The only difference in the multiplet conductivity is the increase of the index \( s \) with \( \omega \).

There are no anomalies in the behavior of \( \text{Re} \sigma(f) \) and \( \text{Im} \sigma(f) \) graphs (Fig.2(a)). However, the relations \( \phi(f) \) (Fig.2 (b)) have maxima for all compositions, so the relation \( \phi(f) = \text{Im} \sigma / \text{Re} \sigma \) seems to be most appropriate for the analysis of the conductivity. The presence of the maximum on the graph of \( \phi(f) \) indicates that the dielectric losses are due to the relaxation nature of hopping transport.

5. Conclusion

The influence of the conductivity on the low frequency dielectric spectra for the compositions \( \text{Bi}_{1.6}\text{Ti}_2\text{Cr}_{0.16}\text{O}_{6.6}, \text{Bi}_{1.55}\text{Ti}_{1.97}\text{Cu}_{0.78}\text{O}_7 \) and \( \text{Bi}_4\text{Ti}_2\text{Fe}_1\text{O}_{11.5} \) was observed experimentally. A suggestion on the hopping type mechanisms of conductivity was deduced relying on the frequency dependence analysis. In the frequency range with weak dependence of \( \phi(f) \), hopping carrier occur in clusters of intermediate size (with a small, though greater than two number of sites). In the range where \( \phi(f) \) increases with frequency, the hopping conductivity is realized in the clusters having large though finite size. For the region where \( \phi(f) \) decreases with increasing the frequency, the conductivity is realized by a two-site hopping.

References

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