FEATURES OF ACOUSTIC PROPERTIES OF CERAMICS $BaLa_2Ti_4O_{12}$ IN THE TEMPERATURE RANGE 100—300 K

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For samples of $BaLa_2Ti_4O_{12}$ ceramics, the results of investigations of the temperature dependences of the propagation velocity and absorption coefficient of longitudinal ultrasonic waves in the temperature range $T = 100$—300 K are reported. The discovered anomalies of acoustic properties are explained by the existence of a "bearing"-type phase transition at the temperature $T \approx 205$ K. Structural aspects of the $BaLa_2Ti_4O_{12}$ lattice rearrangement that can cause such a transition are analyzed.

The clarification of physical mechanisms, which are responsible for dielectric properties of ceramic materials, is interesting for both fundamental science and for their practical applications. In particular, different types of ceramics are the base of modern electronic devices of the ultrahigh frequency range. For the practical application of ceramic materials, it is important that, at a given value of permittivity, they should possess low dielectric losses and the temperature coefficient (TC) of permittivity (TC $\varepsilon' = (1/\varepsilon')d\varepsilon'/dT$) to be close to zero in wide temperature and frequency ranges.

The materials obtained on the base of the triple system BaO—TiO_2—Ln_2O_3(Ln — rare earth element) are ceramics with the properties mentioned above. It was established that the materials with the general formula $BaLn_2Ti_4O_{12}$(barium lanthanoid tetratitanates (BLT)) are formed for all elements of the cerium subgroup and have a complicated crystal structure with perovskite-like fragment as a base [1]. The structure of such compounds is noncentrosymmetric and can be referred to the spatial group *Pba2*. A rather high value of permittivity ($\varepsilon' \approx 100$), low values of the dielectric losses ($\mathrm{tg}\delta < 10^{-3}$), and their minor change in a wide temperature range are the features of dielectric properties of BLT. The temperature coefficient of the permittivity for these substances monotonically changes with increase of the ordinal number of a rare earth element from $-700\cdot10^{-6}$ K^{-1} for $BaLa_2Ti_4O_{12}$ to $+60\cdot10^{-6}$ $K^{-1}$for $BaEu_2Ti_4O_{12}$ [2]. High values of the permittivity of BLT indicate a considerable polarizability of the lattice of these substances. As is known, compounds with the perovskite structure and high polarizability of a lattice have a rather strong temperature dependence of ε' (for example, paraelectric $SrTiO_3$ [3]) or a ferroelectric state in the certain temperature range.

Dielectric spectroscopy investigations of the physical properties of BLT in the wide temperature range have not indicated a phase transition to the ferroelectric state [2, 4] in BLT. At the same time, there were registered some anomalies for $BaLa_2Ti_4O_{12}$ in the temperature dependences of permittivity and dielectric losses. Experimental data from work [2] point to the possibility of a phase transition for the ceramics at the temperature $T \approx 120$ K; and the anomalies discovered for $BaLn_2Ti_4O_{12}$ (Ln = La, Pr, Nd) at liquid-helium temperatures have a relaxation character in accordance with data from [4]. Thus, the problem of the existence of phase transitions in BLT needs further investigations. As is known, acoustic properties of ceramics are very sensitive even to a very slight rearrangement of their lattice. That's why in this work, we have carried out the investigations of the temperature dependences of the absorption coefficient of longitudinal ultrasonic waves (LUV) for $BaLa_2Ti_4O_{12}$ in the temperature range $T = 100 \div 300$ K.

Materials for our samples were obtained by chemical deposition from salt solutions with a further thermal treatment of the sediment. Samples of parallelepiped shape with dimensions $4.5 \times 4.5 \times 5.0$ mm^3 were made of synthesized ceramic powders by hydraulic pressing. The samples firstly were baked to the state with zero water absorption. Measurements of the absorption coefficient and the propagation velocity of ultrasound were carried out in accordance with standard techniques using piezoelectric quartz converters [5].

For the $BaLa_2Ti_4O_{12}$ samples, the temperature dependences of the absorption coefficient $\Delta\alpha(T)$ and propagation velocity $v(T)$ of the longitudinal ultrasonic

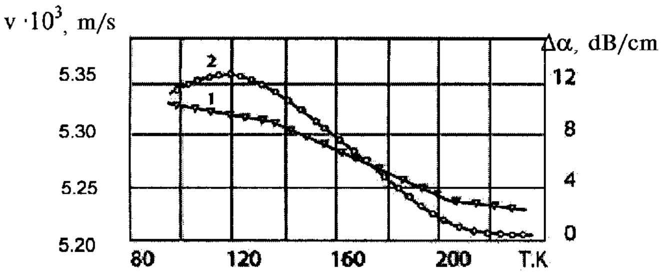

Fig. 1. Temperature dependences of velocity (*1*) and the absorption coefficient (*2*) of longitudinal ultrasonic waves in $BaLa_2Ti_4O_{12}$ at a frequency of 9.5 MHz

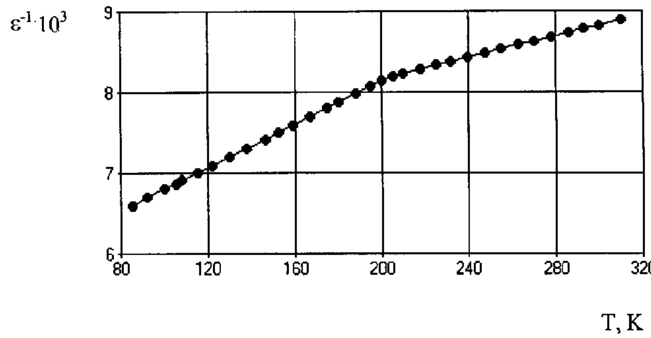

Fig. 2. Temperature dependence of the reciprocal permittivity of $BaLa_2Ti_4O_{12}$ at a frequency of 10 MHz

waves are shown in Fig. 1; they were obtained at a frequency of 9.5 MHz. As is seen, there are two breaks at $T \approx 135$ and 205 K on the temperature dependence of the propagation velocity of ultrasonic vibrations. The latter peculiarity on the $v(T)$ dependence coincides with the break discovered on the temperature dependence $\varepsilon'(T)$ of the permittivity of the same samples $BaLa_2Ti_4O_{12}$ (Fig. 2): they both occur at the same temperature. Since the ultrasound velocity in solids is determined by their elastic moduli, the $v(T)$ dependences are very sensitive to the rearrangement of the crystal structure of these solids. That is why we can expect that the discovered breaks are conditioned by structural phase transitions.

To test this hypothesis, the investigations of a structure behavior of $BaLa_2Ti_4O_{12}$ were carried out in the temperature range $100 \div 300$ K by X-ray diffraction. Namely, using an X-ray diffractometer of the original design by the Debye—Scherer technique (Mo K_α-line, a graphite filter), diffractograms of the $BaLa_2Ti_4O_{12}$ samples were obtained at the temperatures $T_1 = 100$ K and $T_2 = 295$ K. An analysis of the obtained diffractograms did not show up a change of the symmetry of the $BaLa_2Ti_4O_{12}$ unit cell. However, it can be explained by fact that possible changes in the $BaLa_2Ti_4O_{12}$ structure at a decrease of temperature from room one to $T = 100$ K are less than the resolution of the used X-ray device. Such changes of the structure can be caused by the "bearing"-type phase transition. As is known, such transitions (described in detail, for example, in [6]) don't result in an essential rearrangement of the phonon spectrum of ceramics and most often appear as breaks on the temperature dependences of their permittivity.

Structural peculiarities of $BaLn_2Ti_4O_{12}$ compounds indicate a potential possibility of the existence of such transitions. According to [7], the perovskite-like structure of BLT has elements which are specific of tetragonal tungsten bronzes and are characterized by the presence of hollows — structural vacancies in the barium sublattice. The presence of such vacancies can result in that fact that the perovskite structure becomes integrally unstable. For example, lanthanum metatitanate $La_{2/3}\square_{1/3}TiO_3$ ($\square$ is a vacancy), which is crystallized to the perovskite structure, is in the metastable state due to a high concentration of vacancies in the La sublattice at room temperature. At the temperature that exceeds $T = 1100$ K, it decays into $La_2Ti_2O_7$ and TiO_2[8]. "Bearing"-like phase transitions in BLT compounds, which are similar to lanthanum metatitanate ($BaLa_2Ti_4O_{12}$ can be written as $Ba_{1/4}La_{1/2}\square_{1/4}TiO_3$), can be treated as a slight jump-like rearrangement of some structural group. After the rearrangement, the crystal symmetry remains the same. By the analogy with [6], oxygen octahedrons can be such structural groups. Under cooling, the parameters of the unit cell of ABO_3 perovskite decrease and, at a certain temperature, the initial location of ions in the chain —O—B—O— becomes impossible. That is why the "bearing"-like phase transition occurs, which results in the formation of the zigzag chains of oxygen octahedrons [6]. Since changes in the $BaLa_2Ti_4O_{12}$ crystal structure are rather minor during such a rearrangement, the absorption of ultrasonic waves practically is not changed.

The anomalous behavior of the temperature dependence of the absorption of ultrasonic vibrations, which is observed for $BaLa_2Ti_4O_{12}$ samples in the temperature range $T = 120 \div 205$ K (Fig. 1), can be explained by anisotropy of some crystallites and their disordered orientation [9]. Relaxation processes can be another cause of such a behavior of the absorption of ultrasonic waves and the appearance of a break on the temperature dependence of the velocity at $T \approx 135$

K in $BaLa_2Ti_4O_{12}$. Indeed, as was mentioned above, the dielectric relaxation is observed at the liquid-helium temperatures in $La_2Ti_4O_{12}$ in the radio-frequency range [4]. The anomalous damping of electromagnetic oscillations of the submillimeter range discovered by the authors of work [2] is concerned probably with the same relaxation process. It is possible that just this process causes also the anomalous absorption of ultrasonic waves in $BaLa_2Ti_4O_{12}$.

Thus, the obtained experimental data prove that, in $BaLa_2Ti_4O_{12}$, there exist the "bearing"-type phase transition at the temperature $T \approx 205$ K and the relaxation processes which were observed earlier in the radiofrequency range in [2]. The latter condition should be taken into account upon developing the microwave ceramics based on BLT. In this case, to achieve the desired parameters of ceramic materials, solid solutions with a partial substitution in the Ba or Ln sublattice are used (see, for example, [10]). As a consequence of such a substitution, anomalies in the $\varepsilon'(T)$ and tg$\delta(T)$ dependences can shift into the working temperature range, which can result in a significant degradation of dielectric parameters of ceramic materials. Particularly, it can be a source of additional dielectric losses and a deviation of TC ε' from the anticipated value.

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ОСОБЛИВОСТІ АКУСТИЧНИХ ВЛАСТИВОСТЕЙ КЕРАМІКИ $BaLa_2Ti_4O_{12}$ В ІНТЕРВАЛІ ТЕМПЕРАТУР $100 \div 300$ К

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Р е з ю м е

Для зразків кераміки $BaLa_2Ti_4O_{12}$ наведено результати дослідження температурних залежностей швидкості поширення та коефіцієнта поглинання поздовжніх ультразвукових хвиль в інтервалі температур $100 \div 300$ К. Виявлені аномалії акустичних властивостей пояснено наявністю при температурі $T \approx 205$ К фазового переходу типу "зім'яття". Проаналізовано структурні аспекти перебудови кристалічної решітки $BaLa_2Ti_4O_{12}$, що можуть зумовити виникнення такого переходу.