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Short Communication

Dielectric Properties of the Low-temperature Phase Transitions in Divalent Nitrates

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The paper is devoted to the elucidation of realization mechanism of the low-temperature phase transitions in divalent nitrates $Pb(NO_3)_2$, $Sr(NO_3)_2$ and $Ba(NO_3)_2$. The investigations results of dielectric permeance ε and tangent of dielectric losses angle tgδ temperature dependencies are presented for lead nitrate $Pb(NO_3)_2$. The investigations confirm supposition that low-temperature phase transitions in divalent nitrates occurs because of "freezing" of reorientational oscillations of NO_3^- groups around Nitrogen atom, which occur at room temperature. A maximum in $Pm3 \rightarrow P2_13$ phase transition region is observed on the $\varepsilon(T)$ curves. This maximum decreases with increasing of frequency and at 10 KHz frequency becomes like a "step" by it's form. Two maximums are observed on the tg$\delta(T)$ curves. First of them occurs at the phase transition temperature, another one is moved to low-temperature region. The conclusion, that the first maximum of tgδ is connected with NO_3^- groups relaxation and second maximum is connected with a formation of domain structure is made. The energy of activation is calculated by the removing of dielectric permeance maximum and this energy is higher than 2 eV. Such value of activation energy is proper for heavy ions. This fact confirms a supposition, that a relaxation of NO_3^- groups occur at 1 KHz-10 KHz frequencies in the phase transition region.

Keywords: Phase transitions, Divalent nitrates, Dielectric permeance, Tangent of dielectric losses angle, Temperature dependencies.

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1. HISTORICAL REFERENCE

As we established earlier [1], in the divalent nitrates $Pb(NO_3)_2$, $Sr(NO_3)_2$ and $Ba(NO_3)_2$, a chain of $Pm3 \leftrightarrow Pa3 \leftrightarrow P2_13$ phase transitions occurs. Phase transition $Pm3 \rightarrow Pa3$ is distinctly translational and occurs with translation loss along a one of the main directions of the cubic cell. This phase transition is accompanied by increasing of elementary cell in eight times [1]. Phase transition $Pm3 \rightarrow P2_13$ occurs with a loss of inversion center and is the phase transition of remove type [1].

Phase transitions $Pm3 \rightarrow Pa3$ occur at high temperatures.

The low-temperature phase transitions $Pm3 \rightarrow P2_13$ occurs near the temperature of 245 K for lead nitrate $Pb(NO_3)_2$, 235 K for strontium nitrate $Sr(NO_3)_2$ and 225 K for barium nitrate $Ba(NO_3)_2$ and occur with the loss of the inversion center [2]; high-temperature phase transitions $Pm3 \rightarrow Pa3$ occur at the temperature 450-500 K for lead nitrate, 550-600 K for strontium nitrate and 400-425 K for barium nitrate (phase transition temperatures were established using dielectric measurements), are purely translational and are accompanied by loss of translation along the main directions of the cube cell [1]. We determined that phase transition $Pm3 \rightarrow Pa3$ is typical for nonferroics, and phase transition $Pm3 \rightarrow P2_13$ is typical for higher-order ferroics [1]. Thus, according to the symmetrical classification of phase transitions presented in [2, 3], divalent nitrates are higher-order ferroics and nonferroics simultaneously.

Throughout the temperature range of its existence, the $Pb(NO_3)_2$, $Sr(NO_3)_2$, and $Ba(NO_3)_2$ crystals remain cubic and there are no phase transitions except of the mentioned above [1].

It's known [1], that at room temperature divalent nitrates have enormous values of piezooptic coefficients, therefore these crystals can be used in piezooptic transducers. According to our supposition [1], the chain of phase transitions and especial mobility of NO_3 – groups in divalent nitrates are leading to the enormous values of piezooptic coefficients in these crystals.

2. RESEARCH OBJECTIVE

In one of the earlier papers [1] we have investigated temperature dependencies of SHG signal in divalent nitrates at low temperatures. Low-temperature phase $P2_13$ hasn't inversion center. Phase transition $Pm3 \rightarrow P2_13$ occurs with a loss of inversion, so it seems piezoelectric effect to be in $P2_13$ phase. Proceeding from the tensor of piezoelectric coefficients symmetry, in 23 group only the component π_{123} (π_{14}) is nonzero. But we didn't find a piezoelectric effect in $P2_13$ phase. Instead of this by signal SHG temperature investigations we found that a component χ_{123} (χ_{14}) of quadratic susceptibility tensor is nonzero [1]. Probably, this component is the parameter of order of $Pm3 \rightarrow P2_13$ phase transition in divalent nitrates. The forms of temperature dependencies $\chi_{14}(T)$ indicate, that $Pm3 \rightarrow P2_13$ phase transitions described by Landau theory. As issued from the form of these curves, phase transition $Pm3 \rightarrow P2_13$ seems to be the phase transition of first order with the features of second order phase transition.

Based on [4] we supposed, that "freezing" of oscillations of NO_3^- groups around the Nitrogen atom leads to this phase transition. To confirm this supposition and clear the relaxation character of NO_3^- groups it's necessary to investigate temperature dependencies of dielectric permeance and tangent of dielectric losses angle at different frequencies.

3. INVESTIGATION METHODOLOGY OF DIELECTRIC PERMEANCE AND TANGENT OF DIELECTRIC LOSSES ANGLE TEMPERATURE DEPENDENCIES

3.1 Method of Samples Preparation

For the investigations the lead nitrate $Pb(NO_3)_2$ single crystals of a good quality were used. The crystals were grown from the water solutions of lead nitrate salt by spontaneous crystallization method. The saturation of solutions was achieved by decreasing of temperature to 285-290 K or by slowly evaporation at room temperature. The samples were fabricated from single crystals with a developed face (111) by grinding on a batiste moistened with distilled water or on abrasive powders No 7 and No 5 with addition of machine oil. In the final form of the samples was the plane-parallel plates, the thickness of which was in 0.5-1.5 mm interval. The samples were covered by Platinum electrodes by vacuum dusting.

3.2 Methodology of Experiment

The dielectric permeance and tangent of dielectric losses angle measurements in 10^2-10^4 Hz interval of frequencies were carried out by E8-2 bridge with external generator ZG-34 and external indicator. The samples were located inside cryostat and culled by liquid Nitrogen steam. Electric tension between electrodes wasn't higher than 1 V. The measurements were carried out under the gradual heating of samples.

4. RESULTS OF THE EXPERIMENTS AND THEIR DISCUSSION

The temperature dependencies of dielectric permeance and tangent of dielectric losses angle for $Pb(NO_3)_2$ samples of [111] orientation are presented at Fig. 1.

In lead nitrate case the dielectric permeance dispersion near the low-temperature phase transition is like to dispersion of dielectric permeance in complicated Perovskites with nonprecise phase transitions [5].

In complicated Perovskites crystals maximum of dielectric permeance phase transition is observed too. This maximum decreases with increasing of temperature, and at the same time moves to high-temperature region. It's known [5], that in Perovskites the phase transitions of remove type occur, and such behavior of dielectric permeance is explained by relaxation phenomenon, which connected with so-called Kentzig regions.

According to [5], Kentzig regions are the smallest regions in crystal, in which spontaneous polarization is appearing and disappearing periodically near of phase transition, because of heaty fluctuations. In lead nitrate case similar dispersion in phase-transition region can be explained by NO_3^- groups relaxation. As a relaxation we understand reorientational oscillations of NO_3^- groups as a whole ion around the third order axis at first, and periodical removing of Nitrogen atom relatively to three atoms of Oxygen plain at second. This removing lead either to plain or to pyramidal form of NO_3^- group. The activation energy, which we calculated from the value of maximum of dielectric permeance removing, is rather high, it's bigger than 2 eV. This fact confirms the supposition about relaxation of NO_3^- groups near of the phase transition at 1 KHz frequency, because such values of activation energy are proper for heavy ions.

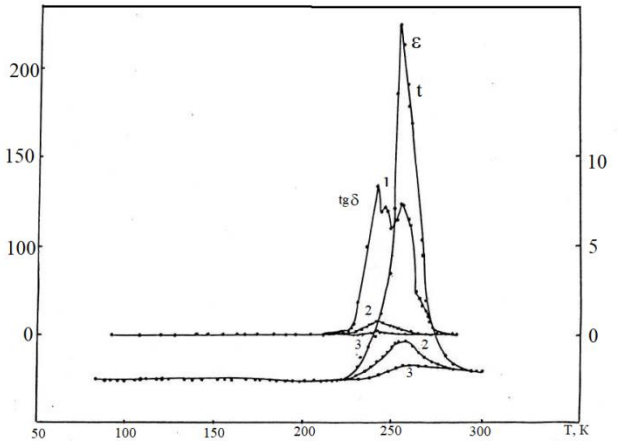

Fig. 1 – Temperature dependences of dielectric permeance ε (left axis) and tangent of dielectric losses angle tgδ (right axis) for lead nitrate $Pb(NO_3)$ crystals of [111] orientation under electric field frequencies KHz (1), 5 KHz (2) and 10 KHz (3)

Interesting peculiarity for investigated crystals is observing of two maximums on the tangent of dielectric losses angle temperature dependencies. First of them occurs at the phase transition temperature, second one is removed to low-temperature region. With increasing of frequency first maximum disappears (it's not observed already at 10 KHz frequency), second one decreases and doesn't change (or nearly doesn't change) it's location on temperature scale. In divalent nitrates case it seems to be that maximum of tgδ, which observed in low-temperature region is connected with domain structure formation. Other maximum of tgδ, which coincides with maximum of ε by temperature (phase transition temperature) seems to be connected with NO_3^- groups relaxation. It's gradual disappearing with frequency increasing indicates about switching of dielectric losses, connected with heaty polarization, stimulated by reorientational oscillations of NO_3^- groups around third order axis.

5. CONCLUSIONS

The temperature dependencies of dielectric permeance ε and tangent of dielectric losses angle tgδ for lead nitrate samples at low temperatures were investigated. The anomalies of $\varepsilon(T)$ and tg$\delta(T)$ curves in the $Pm3 \rightarrow P2_13$ phase transition region were found. In this region the dispersion of dielectric permeance for lead nitrate is similar with dielectric permeance dispersion for the case of complicated Perovskites with nonprecise phase transitions. Such dispersion in phase transition region may be explained by NO_3^- groups relaxation. It's confirmed by activation energy value (2 eV) we calculated, which is proper for heavy ions. These investigations confirm our supposition, that during the transition from Pa3 phase to $P2_13$ phase reorientational oscillations of NO_3^- groups around Nitrogen atom are "freezing". This result doesn't contradict the conclusion we formulated earlier, that $Pm3 \rightarrow P2_13$ phase transition is the phase transition of first order with the features of second order phase transition. This phase transition can be described by Landau theory.

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Діелектричні властивості низькотемпературних фазових переходів в нітратах двовалентних елементів

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Робота присвячена з'ясуванню механізму реалізації низькотемпературних фазових переходів в нітратах двовалентних елементів. Надані результати досліджень температурних залежностей діелектричної проникності ε та тангенсу кута діелектричних втрат tgδ в області низьких температур для нітрату свинця. Ці дослідження підтверджують припущення, що було зроблене раніше, про те, що низькотемпературні фазові переходи $Pm3 \rightarrow P2_13$ в нітратах двовалентних елементів відбуваються завдяки «заморожуванню» реорієнтаційних коливань груп NO_3^- навкруги атому азоту, які відбуваються при кімнатній температурі. На кривих $\varepsilon(T)$ знайдений максимум в області фазового переходу $Pm3 \rightarrow P2_13$, який зменшується із збільшенням частоти та при частоті 10 КГц має вигляд «сходинки». На кривих tg$\delta(T)$ знайдені два максимуми. Перший максимум здійснюється при температурі фазового переходу, другий – зсунутий в область низьких температур. Зроблений висновок, що перший максимум tgδ пов'язаний з релаксацією груп NO_3^-, другий – з формуванням доменної структури в нітратах двовалентних елементів. Енергія активації, що була підрахована за зсувом діелектричної проникності складає величину, більшу ніж 2 еВ. Така енергія активації є характерною для важких іонів. Це підтверджує той факт, що на частотах 1 КГц-10 КГц в області фазового переходу відбувається релаксація груп NO_3^-.

Ключові слова: Фазові переходи, Нітрати двовалентних елементів, Діелектрична проникність, Тангенс кута діелектричних втрат, Температурні залежності.