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Short Communication

Searching for Order Parameter of Low-temperature Phase Transitions in Divalent Nitrates

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The paper is devoted to the searching for order parameter of low-temperature phase transitions in divalent nitrates $Pb(NO_3)_2$, $Sr(NO_3)_2$ and $Ba(NO_3)_2$. According to the curves of temperature dependencies of the quadratic susceptibility tensor component χ_{14}, the conclusion is made that the low-temperature phase transitions in divalent nitrates are the phase transitions of the first order with the features of the second order. The mechanisms of the low-temperature phase transitions in divalent nitrates are discussed from this perspective.

Keywords: Phase transitions, Divalent nitrates, Order parameter, Quadratic susceptibility, Signal intensity of second harmonic generation.

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1. HISTORICAL REFERENCE

It's known that barium, strontium and lead nitrates ($Ba(NO_3)_2$, $Sr(NO_3)_2$ and $Pb(NO_3)_2$) have enormously high level of piesooptic coefficients, therefore these materials may be used for constructing piesooptic transducers [1].

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 ↔ Pa3 ↔ $P2_13$ phase transitions occurs. The low-temperature phase transitions Pm3 → $P2_13$ occur near the temperature of 245 K for lead nitrate $Pb(NO_3)_2$, near 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 [1]. High-temperature phase transitions Pm3 → Pa3 occur at a temperature of 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 accompanied by loss of translation along the main directions of the cube cell [1].

Thus, according to the symmetrical classification of phase transitions presented in [2], divalent nitrates are higher-order ferroics and nonferroics simultaneously.

Throughout the temperature range of their 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 for the mentioned above [4].

2. RESEARCH OBJECTIVE

Since the phase transitions Pm3 → Pa3 are purely translational, the order parameter of these phase transitions must be some microscopic scalar quantity [3]. Such a value can be, for example, the charge density of an electronic cloud formed by free rotation of the NO_3^- groups around the nitrogen atom in the Pm3 phase, followed by a "freezing" of this rotation and its gradual transition to reorientational vibrations of the NO_3^- groups around the nitrogen atom in the $P2_13$ phase [1]. Phase transitions Pm3 → $P2_13$ occur with the loss of the inversion center inside the cubic system, so the order parameter must be the value described by the third-rank tensor [2]. Such a tensor, for example, could be the tensor of piezoelectric coefficients π_{ijk}; however, we did not find the piezoelectric effect in the $P2_13$ phase. This is due to the accumulation of charges along the walls of translational twins in the phase Pa3, which upon transition to the $P2_13$ phase compensate each other, that makes impossible the observation of the piezoelectric effect in the noncentrosymmetric $P2_13$ phase. We were able to visualize these translational twins by etching, and specific etching figures, whose microphotographs are given in [3], were observed in the case of all three compounds.

It is possible to make the assumption that the order parameter of the low-temperature phase transitions Pm3 → $P2_13$ in divalent nitrates is the tensor of the quadratic susceptibility χ_{ijk}, which is known to be proportional to the square root of the signal intensity of the second harmonic generation and has the same symmetry as the tensor of piezoelectric coefficients.

3. INVESTIGATION METHODOLOGY OF THE SIGNAL INTENSITY SHG TEMPERATURE DEPENDENCE

3.1 Method of Samples Preparation

Crystals of lead, strontium and barium nitrates for the samples preparation were grown from aqueous solutions. In the case of $Sr(NO_3)_2$ and $Ba(NO_3)_2$, the samples were fabricated from single crystals of good optical quality with a developed face (111) by grinding on a batiste moistened with distilled water. In the final form, the samples were plane-parallel plates, the thickness of which did not exceed 1.5 mm. In the case of $Pb(NO_3)_2$, a sample of good optical quality with a developed face (111) was cut from a bulk single crystal with the help of a wet thread. After that both surfaces were ground on abrasive powders No. 10, No. 7 and No. 5 sequentially (machine oil was used as filler); then the sample surfaces were polished with diamond paste ASM 40/28 NOM, ASM 20/14 NOM, ASM 10/7 NOM and ASM 2/1 NOM sequentially until maximum transparency was achieved. The sample was a plane-parallel plate of good optical quality 0.3 mm thick, the linear dimensions of which reached 25 mm.

3.2 Methodology of Experiment

The investigations were carried out using a LTI-701 laser operating in Q-switching mode (average power is 1 W, wavelength is 1.06 microns). The sample was placed in a cryostat constructed for optical studies, which was cooled with liquid nitrogen. The SHG signal recorded by the photoelectric multiplier was output simultaneously to the axis of ordinates of the two-component recorder and to the digital indicator, while the signal from the thermocouple, was fed to the axis of abscissa of the recorder, which registered the temperature of the sample. The accuracy of the measurements was 100 pulses per second, the accuracy of the temperature measurement was 0.05 K.

4. RESULTS OF THE EXPERIMENTS AND THEIR DISCUSSION

Fig. 1 shows the temperature dependences of the signal intensity of the SHG at low temperatures, which are strictly linear in region II. It can be seen from the figure that the SHG signal becomes zero when passing to a more symmetrical phase.

Fig. 2 shows the temperature dependences of the tensor component χ_{14} found from the results presented in Fig. 1, as the square root of the SHG signal intensity.

According to [2], the third-rank tensor for crystals of symmetry 23 has only one non-zero component with indexes 14 (123), therefore orientation samples [111] were chosen for the studies.

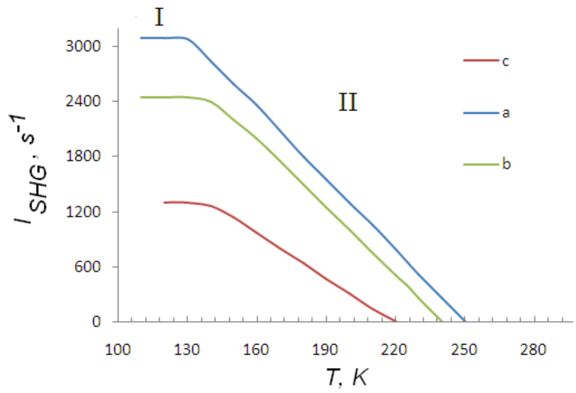

Fig. 1 – Temperature dependences of the SHG signal for single crystals $Pb(NO_3)_2$ (a), $Sr(NO_3)_2$ (b), and $Ba(NO_3)_2$ (c); I – the saturation region; II – linear reduction region

It can be seen from Fig. 2 that the component χ_{14} of the quadratic susceptibility tensor behaves as an order parameter for phase transitions of the first order close to the second [2]. This allows us to judge the nature of the "freezing" of reorientational vibrations of the NO_3– groups around the nitrogen atom near the Pm3 → $P2_13$ phase transition, which occurs gradually. And at the point of the phase transition, the "transformation" happens through "jump" of the form of the NO_3– groups from planar to pyramidal with the nitrogen atom at the apex of the pyramid and three oxygen atoms in its foundation.

Phase 23 was fixed in $Ba(NO_3)_2$ earlier, and the pyramidal form of NO_3^- groups was established by neutron diffraction methods.

For reasons of symmetry, the reconstruction of NO_3^- groups from planar to pyramidal have to lead to the loss of the inversion center upon transition from phase Pa3 to phase $P2_13$.

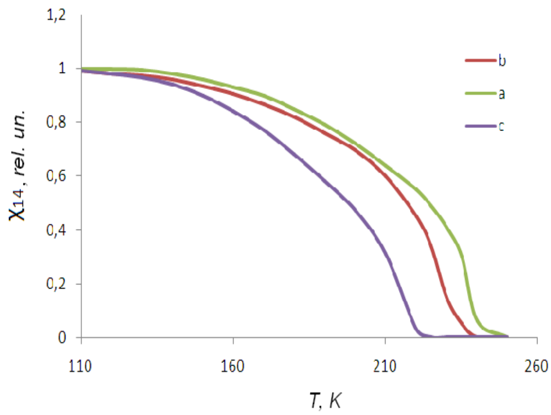

Fig. 2 – Temperature dependence of the χ_{14} component of the quadratic susceptibility tensor χijk for the crystals of $Pb(NO_3)_2$ (a), $Sr(NO_3)_2$ (b) and $Ba(NO_3)_2$ (c)

5. CONCLUSIONS

Because the piezoelectric effect in the noncentrosymmetric low-temperature phase of $P2_13$ in nitrates of strontium, barium and lead is absent, we can consider the order parameter of low-temperature phase transitions in these crystals to be the component χ_{14} of the quadratic susceptibility tensor, which coincides in symmetry with the tensor of piezoelectric coefficients. The temperature behavior of χ_{14} allows to judge low-temperature phase transitions in divalent nitrates as first-order phase transitions close to the second order. In addition, the shape of the $\chi_{14}(T)$ curves makes it possible to judge the nature of the "freezing" of thermal vibrations and the rearrangement of the NO_3^- group shape in the low-temperature phase transitions in lead, strontium and barium nitrates.

To our opinion, high level of piesooptic coefficients in divalent nitrates is connected with especial mobility of NO_3^- groups in these crystals.

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Пошук параметра порядку низькотемпературних фазових переходів в нітратах двовалентних елементів

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У роботі запропоновано вирішення питання про знаходження параметра порядку низькотемпературних фазових переходів в нітратах двовалентних елементів $Pb(NO_3)_2$, $Sr(NO_3)_2$ і $Ba(NO_3)_2$. За формою кривих температурної залежності компоненти тензора квадратичної сприйнятливості χ_{14} зроблений висновок про те, що низькотемпературні фазові переходи в нітратах двовалентних елементів – це фазові переходи першого роду, близькі до другого. З цієї точки зору обговорюється механізм низькотемпературних фазових переходів в нітратах двовалентних елементів.

Ключові слова: Фазові переходи, Нітрати двовалентних елементів, Параметр порядку, Квадратична сприйнятливість, Інтенсивність сигналу ГДГ.