



REGULAR ARTICLE

Phase Transitions and Structural Peculiarities of Divalent Nitrates

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The paper is devoted to the problem of choose of the space group of symmetry for the high temperature phase of divalent nitrates. The photos of reverse lattices of Barium, Strontium and Lead nitrates at room temperature were obtained, as well as at high temperatures, which correlate with the temperatures of realization of high temperature phase in divalent nitrates. The analysis of reflexes indicates, that phase Pa3 realizes at room temperature; at the same time phases Pm3 or Pm3m are to be realized as the high temperature phase. The symmetry considerations, that are described in the paper, testify to Pm3 space group for high temperature phase in divalent nitrates. This phase can be considered as maternity phase for Pa3 and P213 phases, that realizes in divalent nitrates, as it contains all symmetry elements for these phases. So, the chain of phase transitions $Pm3 \leftrightarrow Pa3 \leftrightarrow P213$ can be described by the set of symmetry elements of Pm3 phase. These investigations confirm our supposition, that this chain of phase transitions realizes due to especial mobility of nitrate groups in crystal lattice. It was shown, that high temperature $Pm3 \rightarrow Pa3$ phase transition can be realized because of “freezing” of free move of NO_3 groups around Nitrogen atoms, which has spherical symmetry and turning it into their oscillations around Nitrogen atom in one plane.

Keywords: Phase transitions, Divalent nitrates, Symmetry, Space group, Reflexes, Laue-class.

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1. HISTORICAL REFERENCE

As we mentioned [1], the chain of phase transitions $Pm3 \leftrightarrow Pa3 \leftrightarrow P213$ in divalent nitrates $Pb(NO_3)_2$, $Sr(NO_3)_2$ and $Ba(NO_3)_2$ occurs. The temperatures of high temperature phase transition $Pm3 \rightarrow Pa3$ and low temperature phase transition $Pm3 \rightarrow P213$ are presented in a Table 1.

Table 1 – Temperatures of phase transitions in divalent nitrates

Compound	$Pm3 \rightarrow Pa3$	$Pm3 \rightarrow P213$
$Pb(NO_3)_2$	450 – 500 K	Near 245 K
$Sr(NO_3)_2$	550 – 600 K	Near 235 K
$Ba(NO_3)_2$	400 – 425 K	Near 225 K

The temperatures of $Pm3 \rightarrow Pa3$ phase transitions were obtained by dielectric measurements, while the temperatures of $Pm3 \rightarrow P213$ phase transitions were fined out by SHG signal investigations [1].

As the symmetry of divalent nitrates remains cubic over the whole temperature area of their existence we can make a conclusion, that high temperature phase transition is distinctly translational and occurs with a loss of translation along the main directions of elementary cell, while low temperature phase transition occurs with a loss of inversion center. So, according to the phase transitions classification [2, 3], we made a conclusion, that divalent nitrates are higher order ferroics and nonferroics simultaneously.

As we mentioned earlier [1], at room temperature divalent nitrates have enormous values of piezooptic coefficients, therefore these crystals can be used in piezo-

optic transducers. Such piezooptic behavior of the crystals is probably connected with the existence of phase transitions in these materials.

2. RESEARCH OBJECTIVE

Based on [4], we supposed, that especial mobility of NO_3^- groups is responsible of the chain of phase transitions in divalent nitrates. To our opinion, $Pm3 \rightarrow Pa3$ phase transition occurs because of “freezing” of free rotation of NO_3^- groups around Nitrogen atom. This free rotation has a spherical symmetry. In the Pa3 phase only oscillations of NO_3^- groups around Nitrogen atom realize.

Phase transition $Pm3 \rightarrow P213$ occurs because of “freezing” of NO_3^- groups oscillations. In $P213$ phase NO_3^- groups don’t oscillate and take the form of pyramids with Nitrogen atoms on their tops.

Besides of this, the mobility of nitrate groups leads to enormous values of piezooptic coefficients.

According to the theory of groups, at high temperatures in divalent nitrates can be realized $Pm3m$ phase as well as $Pm3$ phase. These two space groups can describe the symmetry of the maternity phase for divalent nitrates. To elucidate the space group for the maternity phase it’s necessary to implement high temperature photographing of reverse lattices of the crystals and compare the photos at room temperature and at high temperatures.

3. INVESTIGATION METHODOLOGY OF REVERSE LATTICES PHOTOGRAPHING

3.1 Method of Samples Preparation

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For the implementation of experiment the crystals of Lead nitrate $Pb(NO_3)_2$, Strontium nitrate $Sr(NO_3)_2$ and Barium nitrate $Ba(NO_3)_2$ of a good quality were used. These crystals were grown up from the water solutions of the salts by slow evaporation under room temperature. The samples were the needles of [100] orientation. These needles were obtained by the water grinding of the crystals with (100) developed face.

3.2 Methodology of Experiment

The reverse lattices photos of zero order reflection were obtained by the camera of reverse lattice photographing KFOR-1. The wave length of the radiation was $1,5424 \text{ \AA}$ ($K\alpha$ - radiation of Cuprum was used). The Universal Roentgen Spectrometer URS-60 was used as a source of radiation. For high temperature investigations the samples were located to the center of Nickel- Chromium single coil, heated by the current of 6 Amperes, which was regulated by the decreasing transformer. High temperature experiments were implemented without β - filter to register weak reflexes.

4. RESULTS OF THE EXPERIMENTS AND THEIR DISCUSSION

The photo of reverse lattice for Barium nitrate sample of zero order reflection at room temperature and its scheme are presented at Fig. 1.

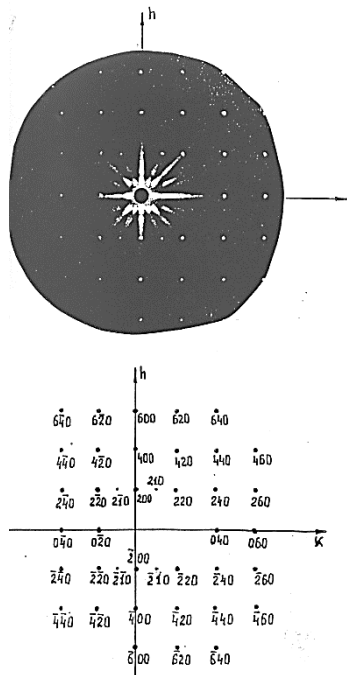


Fig. 1 – The photo of reverse lattice of zero order reflection for Barium nitrate at room temperature and its scheme

The scheme shows, that among $(hk0)$ reflections only the reflections with even h are present. This result confirms, that $Pa3$ phase realizes at room temperature in Barium nitrate. Similar results were obtained for Strontium nitrate and Lead nitrate crystals. At Fig. 2 the photo of reverse lattice of zero order reflection for Bar-

ium nitrate sample at 483-513 K and its scheme are presented. At the scheme we can see the appearing of weak, but distinct reflexes (510) and $(5\bar{1}0)$. These reflexes are forbidden for $Pa3$ space group and indicate the realization of high temperature phase in Barium nitrate, which has higher symmetry than $Pa3$.

Similar results we obtained for Strontium nitrate and Lead nitrate crystals at the temperatures, which lies higher, than high temperature phase transitions (Table 1). In cubic syngony 30 space groups can realize: 12 of them belong to T_h Laue class ($m3$) and 18 belong to O_h Laue class ($m3m$). The new reflexes of $(hk0)$ type with odd h can indicate the realization in high temperature phase only of two of them: $Pm3$ (T_h Laue class) or $Pm3m$ (O_h Laue class). In both cases at high temperature phase transition not only syngony (cubic) but type of elementary cell (primitive) are saved. It's well known, that phase transitions with a saving of cubic primitive are possible only with increasing of elementary cell volume by eight times. Therefore, considering divalent nitrates structure, we must choose one octant elementary cell $Pa3$ as elementary cell of high temperature phase (Fig. 3).

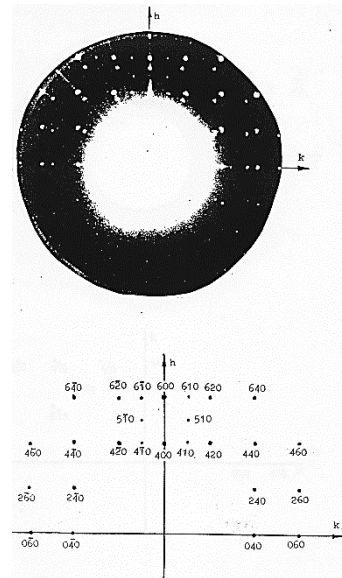


Fig. 2 – The photo of reverse lattice of zero order reflection for Barium nitrate sample at 483-513 K temperatures and its scheme

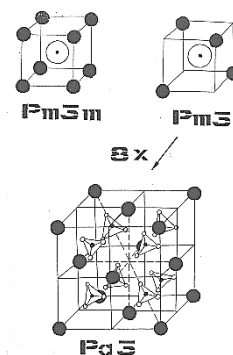


Fig. 3 – The illustration of a possibility of phase transition $Pm3 \rightarrow Pa3$ with an increasing of cell volume by eight times

In one octant of Pa3 elementary cell only four from eight apexes of the cube are occupied by metal atoms. Therefore, high temperature phase in divalent nitrates couldn't be described by space group Pm3m (Fig. 3), as in this case all apexes of elementary cell (octant) are to be occupied by metal atoms, that is impossible for Pa3 group. So, we must choose Pm3 group for high temperature phase in divalent nitrates.

This experiment confirms, that especial mobility of nitrate groups leads to the chain of phase transitions $Pm3 \leftrightarrow Pa3 \leftrightarrow P2_13$ in divalent nitrates. Thus, in Pm3 phase the spherical symmetry of NO_3^- groups rotation around Nitrogen atom take place (Fig. 3). With decreasing of temperature this rotation is "freezing" and turns into oscillation of NO_3^- groups around Nitrogen atom in the plane of Oxygen atoms in Pa3 phase (Fig. 3). As we mentioned earlier [1], low temperature phase transition $Pm3 \rightarrow P2_13$ occurs because of "freezing" of these oscillations as well as plane triangles of NO_3^- groups in Pa3 phase became pyramids with Nitrogen atom on the tops in P2₁3 phase. In this phase 8 NO_3^- groups in the elementary cell are divided into two types (4 + 4). NO_3^- groups of the first type are turned by the top of pyramid (Nitrogen

atom) to the three nearest cations; NO_3^- groups of the second type are turned to the three nearest cations by the basis of pyramid (three Oxygen atoms).

Such symmetry arrangement of NO_3^- groups leads to the absence of inversion center in low temperature P2₁3 phase.

5. CONCLUSIONS

The photos of reverse lattices of Barium nitrate $Ba(NO_3)_2$, Lead nitrate $Pb(NO_3)_2$ and Strontium nitrate $Sr(NO_3)_2$ were obtained at room temperature and at temperatures, which lies higher of the high temperature phase transition $Pm3 \rightarrow Pa3$. At the photos of reverse lattices at high temperatures the reflexes of $(hk0)$ type with odd h- index were observed. These reflexes confirm the realization of Pm3m or Pm3 phase at high temperatures. But, according to symmetry consideration, we choose Pm3 space group as the group, that describes the symmetry of the crystals in high temperature phase. Pm3 phase can be considered as the maternity phase for Pa3 and P2₁3 phases. Pm3 phase describes a chain of phase transitions $Pm3 \leftrightarrow Pa3 \leftrightarrow P2_13$, which realizes in divalent nitrates.

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Фазові переходи та особливості структури нітратів двовалентних елементів

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Робота присвячена проблемі вибору просторової групи симетрії для високотемпературної фази нітратів двовалентних елементів. Були отримані фотографії зворотних ґраток нітратів барію, стронцію та свинцю при кімнатній температурі, так само як і при високих температурах, які відповідають температурам реалізації високотемпературної фази в нітратах двовалентних елементів. Аналіз рефлексів показав, що при кімнатній температурі реалізується фаза Pa3, у той час як при високих температурах повинна реалізуватися фаза Pm3 або Pm3m. Згідно з міркуваннями симетрії, які були викладені у роботі, в високотемпературній фазі нітратів двовалентних елементів повинна реалізуватися фаза Pm3. Ця фаза може бути розглянута, як материнська фаза для фаз Pa3 та P2₁3, що реалізуються в нітратах двовалентних елементів, оскільки вона містить всі елементи симетрії цих фаз. Таким чином низка фазових переходів $Pm3 \leftrightarrow Pa3 \leftrightarrow P2_13$ може бути описана набором елементів симетрії, що містить фаза Pm3. Дослідження підтверджують наше припущення, що ця низка фазових переходів здійснюється завдяки особливій рухливості нітратних груп у кристалічній ґратці. Було показано, що високотемпературний фазовий перехід $Pm3 \rightarrow Pa3$ може бути реалізований завдяки «заморожуванню» вільного руху груп NO_3^- навкруги атомів азоту, який має сферичну симетрію та обертається у їхнє коливання навкруги атому азоту в одній площині.

Ключові слова: Фазові переходи, Нітрата двовалентних елементів, Симетрія, Просторова група, Рефлекси, Лауе-клас.