



## REGULAR ARTICLE

### Translational Twins and Extraordinary Classification of Divalent Nitrates

A.G. Kolomoets\* , O.V. Shkola, L.O. Lisina, O.Ya. Kuznetsova

*Berdiansk State Pedagogical University, 69011 Zaporizhia, Ukraine*

(Received 10 January 2025; revised manuscript received 18 April 2025; published online 28 April 2025)

Symmetry aspects of  $Pm\bar{3} \rightarrow Pa\bar{3}$  and  $Pm\bar{3} \rightarrow P2_1\bar{3}$  phase transitions in Barium, Strontium and Lead nitrates are considered. It is noted that the  $Pm\bar{3} \rightarrow Pa\bar{3}$  phase transition is proper for crystal class called nonferroics. The characteristic features of nonferroics are given. It has been shown that divalent nitrates have these features. The  $Pm\bar{3} \rightarrow P2_1\bar{3}$  phase transition is classified as a phase transition characteristic of second-order ferroics. Thus, it is concluded that divalent nitrates are second-order ferroics and nonferroics at the same time. It was reported that according to the classification of higher-order ferroics, a spontaneous thermodynamic quantity described by a third-rank tensor should arise in the  $P2_1\bar{3}$  phase. Such a tensor could be a tensor of piezoelectric coefficients, but in the  $P2_1\bar{3}$  phase we were unable to detect the piezoelectric effect. It was suggested that in the  $P2_1\bar{3}$  phase piezoelectric charges are localized on the walls of translational twins (domains), where they can be neutralized. Such domains arise as a result of the  $Pm\bar{3} \rightarrow Pa\bar{3}$  phase transition. They were visualized by chemical etching. The temperature dependences of dielectric permeance in high-temperature region were also investigated. Small anomalies of the dielectric permeance were found in the vicinity of the  $Pm\bar{3} \rightarrow Pa\bar{3}$  phase transition for all three compounds. It is noted that such anomalies are one of the signs of translational phase transitions.

**Keywords:** Phase transitions, Divalent nitrates, Ferroics, Nonferroics, Domains, Chemical etching, Dielectric permeance.

DOI: [10.21272/jnep.17\(2\).02009](https://doi.org/10.21272/jnep.17(2).02009)

PACS numbers: 42.70.Mp, 77.84. – s

## 1. INTRODUCTION

As we reported earlier [1], the chain of phase transitions  $Pm\bar{3} \leftrightarrow Pa\bar{3} \leftrightarrow P2_1\bar{3}$  in Strontium  $Sr(NO_3)_2$ , Barium  $Ba(NO_3)_2$  and Lead  $Pb(NO_3)_2$  nitrates takes place. These phase transitions occur with a saving of cubic cell.  $Pm\bar{3} \rightarrow Pa\bar{3}$  phase transition belongs to high-temperature region, when  $Pm\bar{3} \rightarrow P2_1\bar{3}$  phase transition realizes at low temperatures.

The consideration of symmetry aspects of these phase transitions shows, that  $Pm\bar{3} \rightarrow Pa\bar{3}$  phase transition is proper for a crystal class, which has name of nonferroics. It means, that one or more partitive translations must arise in a low-temperature phase; and spontaneous thermodynamic value, that appears as a result of this phase transition is microscopical one.

It's known [2], that nonferroic crystals have three next peculiarities.

At first, only anti-phase domains are to be observed in a low-symmetry phase.

At second, macroscopic variables wouldn't spontaneously appear in the vicinity of phase transition, due to the saving of point symmetry. Different anomalies of physical characteristics of nonferroics will manifest as anomalies of macroscopic values, which exist in original phase.

And at third, one of the factors that indicates a realization of translational phase transition is a presence of superstructural reflections on reverse lattice photos. At

the same time, the reflections that correspond to the initial phase should not split in the vicinity of phase transition. This is a consequence of point symmetry maintaining at such phase transitions.

As to the first condition, translational twins can be visualized by chemical etching.

Regarding the second condition we can assume, that macroscopic value, that exists in initial phase and anomalies of which we can observe during the transition into dissymmetrical phase, is the dielectric permeance tensor.

At last, according to the third condition, the reflections on the reverse lattice photos, which indicate the initial phase, don't split in the vicinity of  $Pm\bar{3} \rightarrow Pa\bar{3}$  phase transitions [1]. Some of these reflections (permitted for  $Pm\bar{3}$  phase, but forbidden for  $Pa\bar{3}$  phase) during the transition into  $Pa\bar{3}$  phase are disappearing [1].

$Pm\bar{3} \rightarrow P2_1\bar{3}$  phase transition is proper for second order ferroics [2].

It's known [3, 4], that ferroics are the substances, which have some reorientable spontaneous values in some temperature intervals or below some temperatures. These spontaneous values may be vectors (spontaneous polarization, spontaneous magnetization), second rank tensors (spontaneous deformation, dielectric permeance), third rank tensors (piezoelectric modules, quadratic susceptibility), fourth rank tensors (elastic constants), etc. Ferroics of the first, second and higher orders are distinguished, depending on whether one field

\* Correspondence e-mail: [kolombozia@gmail.com](mailto:kolombozia@gmail.com)



or a combination of fields switches one orientation state (domain) to another. So, if switching is carried out under the influence of one of the physical fields (electric, magnetic or mechanical stress), than the crystals belong to first order ferroics (ferroelectrics, ferromagnetics, ferroelastics). If switching is carried out by two fields (for example, electric field + mechanical stress, or mechanical stress + mechanical stress), the crystals belong to second order ferroics (for example, ferroelastoelectrics or ferrobielastics). If such switching is carried out under the influence of three physical fields at once, then the crystals belong to third order ferroics, and so on.

Returning to the  $Pm3 \rightarrow Pa3$  phase transition, in paper [1] we have shown, that the third condition for non-ferroics in divalent nitrates case is satisfied. To check whether the first and second conditions are satisfied for divalent nitrates, we performed experiments on chemical etching of the surface of these crystals at room temperature, and on studying of dielectric permeance temperature dependences in high temperature region.

## 2. INVESTIGATION METHODOLOGY

### 2.1 Methods of Samples Preparation

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 aqueous solutions of the salts by slow evaporation under room temperature.

For the experiments on surface etching crystals with developed faces (111) were used.

For dielectric investigations single crystals with developed faces (111) and (100) were used. In this case the thickness of the samples was reduced by grinding using cambric moistened with distilled water, or using abrasive powders No 7 and No 5 with the addition of machine oil Then Platinum electrodes were applied to the samples using vacuum spraying.

### 2.2 Methodology of Experiments

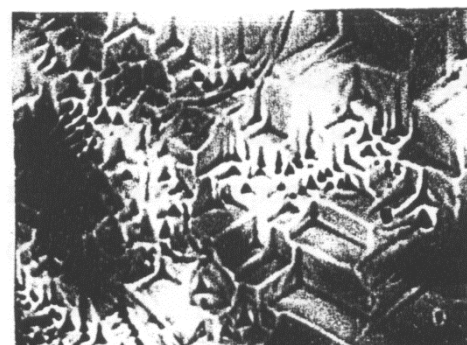
The surface of Lead nitrate, Strontium nitrate and Barium nitrate crystals was studied by etching using optical microscopes MIN-8 and NU-2. Distilled water was used as an etchant for Strontium and Lead nitrate crystals, and glycerin was used for Barium nitrate crystals. The study of the geometry of etching figures was carried out using the MII-4 interferometer.

Dielectric permeance measurements in the frequency range  $10^3$ - $10^6$  Hz were carried out using an E8-2 bridge with an external generator ZG-34 and an external indicator. The voltage between electrodes didn't exceed 1 Volt. The relative error in measuring of the capacitance of the samples was 0.2 %. The temperature was measured with an accuracy of 0.05 K.

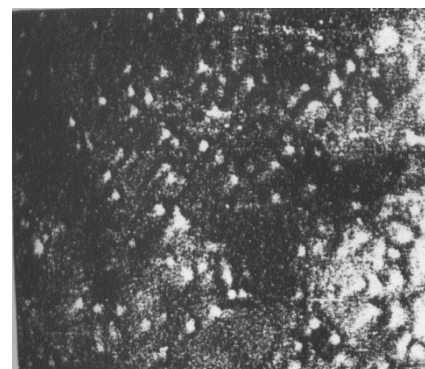
## 3. RESULTS OF THE EXPERIMENTS AND THEIR DISCUSSION

The etching patterns on (111) surfaces for all three compounds are pits in the form of three- wed pyramids, forming a "block" structure (Fig. 1). For Lead nitrate the

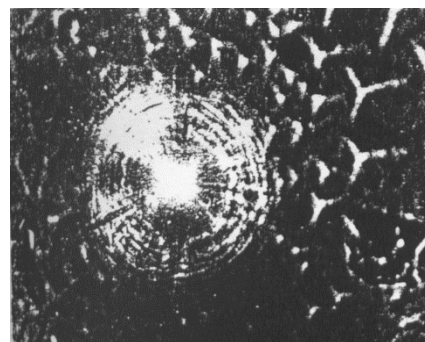
block sizes were several times smaller than for Strontium nitrate. For Barium nitrate they were in order smaller than for Strontium nitrate. For Barium nitrate the block sizes turned out to be so small that they couldn't be detected by etching with distilled water due to high dissolution rate, so glycerin was chosen as an etchant for Barium nitrate. Using an etching method, it was established, that such a "block" structure "grows" trough the crystals, thus patterns similar to those presented on Figure 1, will be repeated at any point in the volume of the crystals. Using the MII-4 interferometer, the geometry of etching pits on the surface of Barium, Strontium and Lead nitrates was studied. It was found that the apex angle of the trihedral pyramids obtained on (111) surface for all three compounds ranges from  $114^\circ$  to  $117^\circ$ , and this difference is withing the measurement error of the interferometer.



a)



b)

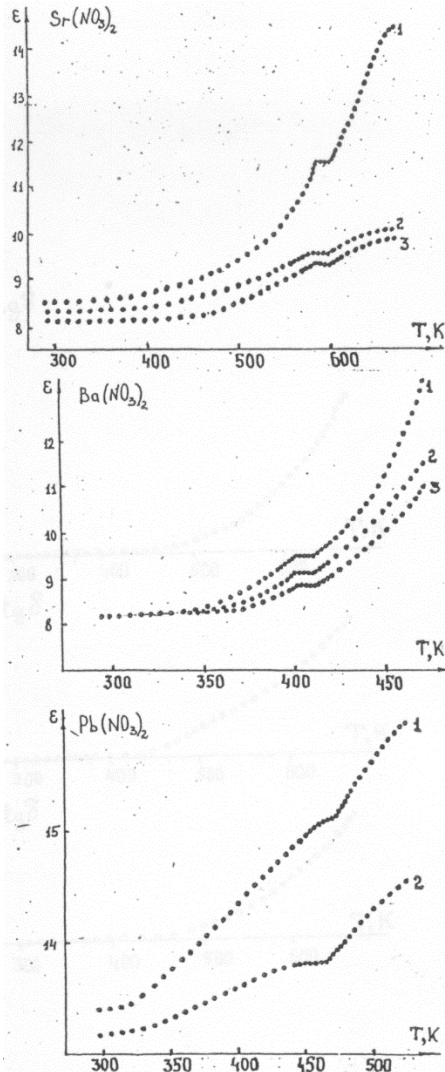


c)

**Fig. 1** – The surface etching patterns of the crystals of: a) Strontium nitrate, magnification 72; b) Lead nitrate, magnification 150; c) Barium nitrate, magnification 1000

It should be noted that such a “block” structure of divalent nitrates can’t be associated with the mechanism of crystal growth, since it is known that these crystals grow as a result of the developing of spiral dislocations on their surface. We discovered such dislocations, but their observation was possible at magnifications several orders lower than the observation of the “block” structure.

The temperatures of high-temperature  $Pm3 \rightarrow Pa3$  phase transitions were established using the temperature dependences of the dielectric permeance (Fig. 2).



**Fig. 2** – The temperature dependences of dielectric permeance for Strontium nitrate, Barium nitrate and Lead nitrate crystals for [100] direction and applied field frequencies 1 KHz (1), 10 KHz (2) and 1 MHz (3)

On Figure 2 the same graph shows cooling curves for different frequencies. For all three compounds, against the background of a monotonic increase of dielectric permeance with increasing of temperature, small anomalies in the form of a “plateau” are observed. The location of these anomalies on temperature scale doesn’t depend on the frequency of applied field. The temperatures of these anomalies are in the temperature ranges 403-418 K for Barium nitrate, 463-478K for Lead nitrate and 588-603 K for Strontium nitrate. Evidently,  $Pm3 \rightarrow Pa3$  phase tran-

sitions occur in these temperature ranges. For [111] direction the results are similar for all three compounds, although they are not presented in this paper.

Thus, it can be argued that the first two conditions for nonferroic crystals, mentioned above, are met in the case of divalent nitrates.

The etching patterns we identified on the surface of the crystals may correspond to translational twins arising as a result of  $Pm3 \rightarrow Pa3$  phase transition. As we showed in paper [1], during this phase transition three partitive translations arise along the main directions of the cubic unit cell.

According to the second condition, dielectric permeance temperature dependences show small anomalies in the vicinity of a phase transition.

So, we can define  $Pm3 \rightarrow Pa3$  phase transition as a translational one, and divalent nitrate crystals as nonferroics.

During translational phase transitions a certain microscopic spontaneous quantity should arise in the low-symmetry phase. According to our reasoning, discussed in paper [1], such a spontaneous microscopic quantity may be the density of the electron cloud created by the thermal movement of Oxygen ions around Nitrogen atom.

Considering the low-temperature  $Pm3 \rightarrow P2_13$  phase transition we should note, that this phase transition occurs with the loss of inversion center. The spontaneous thermodynamic quantity, that arise as a result of such a phase transition must be described by a third-rank tensor. Such a tensor could be the tensor of piezoelectric coefficients, but we didn’t observed a piezoelectric effect in  $P2_13$  phase. This may occur due to the fact that piezoelectric charges accumulate on the walls of translational twins, where they can be neutralized.

#### 4. CONCLUSIONS

The two phase transitions, which take place in divalent nitrates were discussed: high-temperature  $Pm3 \rightarrow Pa3$  and low-temperature  $Pm3 \rightarrow P2_13$ . It was shown, that  $Pm3 \rightarrow Pa3$  phase transition is proper for a special crystal class, named nonferroics. During this phase transitions three partitive translations along the main directions of the cubic cell are appearing. Spontaneous thermodynamic value, which is arising at this phase transition is microscopical one. We supposed, that this microscopical value is a density of cloud, that changes because of changing of move character of Oxygen ions around Nitrogen atom in  $NO_3^-$  group. It was shown, that specific domain structure appears during this phase transition. These translational domains were visualized by chemical etching. They are responsible for the absence of piezoelectric effect, which should be observed in  $P2_13$  phase. We made assumption, that piezoelectric charges accumulate on the domain walls, where they are neutralized. Also, we found anomalies on the  $\epsilon(T)$  curves in the vicinity of  $Pm3 \rightarrow Pa3$  phase transitions. These anomalies illustrate one of the conditions that the crystals are to be nonferroics.

$Pm3 \rightarrow P2_13$  phase transition is proper for second rank ferroics. Thus, we conclude that divalent nitrates are ferroics and nonferroics simultaneously. This circumstance distinguishes divalent nitrates from a number of other active dielectrics and makes their further study to be more valuable.

## REFERENCES

1. A.G. Kolomoets, O.V. Shkola, L.O. Lisina, *J. Nano- Electron. Phys.* **16** No 1, 01009 (2024).
2. A. Bussman-Holder, H. Keller, *Ferroelectrics* **613** No 1, 4 (2023).
3. Yu. Poplavko, Yu. Didenko, D. Talanchuk, *Ferroelectrics* **600** No 1, 35 (2022).
4. Yu. Poplavko, Yu. Didenko, D. Talanchuk, *Ferroelectrics* **614** No 1, 145 (2023).

**Трансляційні двійники та незвичайна класифікація нітратів двовалентних елементів**

Г.Г. Коломоєць, О.В. Школа, Л.О. Лісіна, О.Я. Кузнецова

*Бердянський державний педагогічний університет, 69011 Запоріжжя, Україна*

Розглянуті симетрійні аспекти фазових переходів  $Pm3 \rightarrow Pa3$  та  $Pm3 \rightarrow P213$  в нітратах стронцію, барію та свинцю. Відмічено, що фазовий перехід  $Pm3 \rightarrow Pa3$  характерний для кристалічного класу, який має назву «нефероїки». Наведено характерні особливості нефероїків. Показано, що нітрати двовалентних елементів мають такі особливості. Фазовий перехід  $Pm3 \rightarrow P213$  класифіковано, як фазовий перехід, характерний для фероїків другого порядку. Таким чином, зроблений висновок про те, що нітрати двовалентних елементів є нефероїками та фероїками другого порядку одночасно. Було повідомлено, що згідно з класифікацією фероїків вищих порядків, у фазі  $P213$  нітратів двовалентних елементів має спостерігатися п'єзоелектричний ефект, однак нам не вдалося його виявити. Було зроблене припущення, що в фазі  $P213$  п'єзоелектричні заряди локалізовані на стінках трансляційних доменів, де вони можуть бути нейтралізовані. Такі домени (двійники) виникають як результат фазового переходу  $Pm3 \rightarrow Pa3$ . Вони були візуалізовані за допомогою хімічного травлення. Були досліджені температурні залежності діелектричної проникності в області високих температур. Виявлені малі аномалії діелектричної проникності для всіх трьох сполук в околиці фазового переходу  $Pm3 \rightarrow Pa3$ . Відмічено, що такі аномалії є однією з ознак трансляційного фазового переходу.

**Ключові слова:** Фазові переходи, Нітрати двовалентних елементів, Фероїки, Нефероїки, Домени, Хімічне травлення, Діелектрична проникність.