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The effect of barium titanate admixture on the stability of potassium nitrate ferroelectric phase in $(1-x)\text{KNO}_3 + (x)\text{BaTiO}_3$ composites

Olga A. Alekseeva^{a,*}, Alexander A. Naberezhnov^{a,b}, Elena V. Stukova^c, Vadim I. Popkov^d^a Peter the Great St. Petersburg Polytechnic University, 29 Politekhnicheskaya St., St. Petersburg, 195251, Russian Federation^b Ioffe Physical Technical Institute of RAS, 26 Politekhnicheskaya St., St. Petersburg 194021, Russian Federation; Peter the Great St. Petersburg Polytechnic University, 29 Politekhnicheskaya St., St. Petersburg 195251, Russian Federation^c Amur State University, 21 Ignatievskoe Shosse, Blagoveshchensk 675027, Russian Federation^d St. Petersburg Institute of Technology (Technical University), 26 Moskovskiy Ave., St. Petersburg 190013, Russian Federation

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Abstract

The study of temperature evolution of the KNO_3 structure in ferroelectric $(1-x)\text{KNO}_3 + (x)\text{BaTiO}_3$ composites at $x = 0.25$ and 0.50 has been carried out on cooling and on heating using X-ray diffraction. It was shown that on cooling the phase transition temperature (T_c) from the high-temperature paraelectric phase into the ferroelectric one did not depend on barium titanate concentration and practically coincided with T_c for the pure KNO_3 . Simultaneously the admixture of BaTiO_3 essentially enlarged the temperature interval of the KNO_3 ferroelectric phase stability in these composites. Structure refinement did not confirm the suppression of the ferroelectric phase of potassium nitrate proposed previously for $(0.5)\text{KNO}_3 + (0.5)\text{BaTiO}_3$ sample on the basis of dielectric spectroscopy data. The transition from the ferroelectric phase into the low-temperature paraelectric α -phase was not observed in this composite on cooling down to 348 K.

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This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).**Keywords:** Ferroelectric; Composite; Ferroelectric phase transition; X-ray diffraction.

1. Introduction

Ferroelectric composites are a type of inhomogeneous ferroelectric structure consisting of components with different dielectric properties. Macroscopic physical properties of similar systems can significantly differ from the properties of initial components due to mutual effects. It has been shown [1] that the introduction

of long-range coupling interaction in the ferroelectric $\text{PbTiO}_3/\text{BaTiO}_3/\text{PbTiO}_3$ sandwich system leads to an increase in the average BaTiO_3 interlayer spontaneous polarization and to the reduction of size effects on the spontaneous polarization of ferroelectric thin films. An increase of the temperature interval, where an incommensurate phase of NaNO_2 exists in $(1-x)\text{NaNO}_2 + (x)\text{BaTiO}_3$ composites with different BaTiO_3 admixtures, has been found out [2]. A decrease in KNO_3 γ - α phase transition (PT) temperature has been observed [3] in the $\text{KNO}_3 + \text{SiC}$ powder mixtures depending on the interface between the neighboring KNO_3 particles

* Corresponding author.

E-mail addresses: blackhole2010@yandex.ru (O.A. Alekseeva), alex.naberezhnov@mail.ioffe.ru (A.A. Naberezhnov), lenast@bk.ru (E.V. Stukova), vip-07@yandex.ru (V.I. Popkov).

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which can be regulated by varying the SiC powder volume fraction. At the same time the γ - α phase transition slows down. Potassium nitrate KNO_3 at room temperature and at the atmospheric pressure has an orthorhombic structure (space group $Pm\bar{c}n$) [4]. This state is called α -phase or II-phase. The phase transition into the high temperature trigonal phase (β -phase or I-phase, space group $R\bar{3}m$) occurs on heating at $T \approx 401$ K. The ferroelectric KNO_3 phase (γ -phase or III-phase, space group $R3m$) exists at the temperature range of 397–378 K on cooling only [5,6]. This state in the KNO_3 thin films [7] and nanoparticles [8,9] can be stable even below 273 K. These films show promise for use in ferroelectric memory FeRAM devices because of the square hysteresis loop, a low switching voltage value (5 V) and fast switching time (20 ns) [10]. However, KNO_3 has some limitations including the metastability of the KNO_3 ferroelectric phase at ambient conditions [5].

Barium titanate BaTiO_3 is a displacive-type ferroelectric with perovskite structure. Above Curie temperature $T_C = 393$ K BaTiO_3 has a cubic structure (space group $Pm\bar{3}m$). Tetragonal (space group $P4mm$) BaTiO_3 phase exists at cooling down to 278 K where the second phase transition into a rhombic phase occurs and near 183 K the third phase transition into a rhombohedral phase takes place.

Previous studies have discussed the dielectric properties of $(1-x)\text{KNO}_3 + (x)\text{BaTiO}_3$ composites with the BaTiO_3 particles volume fraction $x = 0.05$ – 0.50 [11,12]. The temperature dependence of dielectric permittivity has two maxima on cooling. The first one is observed at the temperature ≈ 400 K corresponding to the β - γ phase transition. The position of this anomaly practically does not depend on BaTiO_3 concentration. The second maximum at the lower temperature shifts significantly with an increase of BaTiO_3 admixture. This maximum has been attributed to the γ - α phase transition in KNO_3 [11,12]. The dependence of the temperature range ΔT , where the KNO_3 ferroelectric phase exists, from BaTiO_3 concentration has been obtained. ΔT grows monotonically from 12 K up to 65 K with an increase of BaTiO_3 concentration from $x = 0$ to 0.4 respectively. At $x = 0.5$ the second maximum has not been observed and the KNO_3 ferroelectric phase has been assumed to be suppressed. To verify this supposition the studies of the temperature evolution of $(1-x)\text{KNO}_3 + (x)\text{BaTiO}_3$ composites structure on cooling and heating have been carried out.

2. Experiment

We have used the powder mixtures of KNO_3 and BaTiO_3 with two different values of the BaTiO_3 volume

fraction: 25 and 50 vol.%. Measurements have been performed using a Shimadzu X-ray diffractometer on the $\text{Cu K}\alpha$ wavelength $\lambda = 1.54 \text{ \AA}$ on heating and cooling in the temperature range of 350–410 K including several temperature points of the KNO_3 phase transitions. The 2θ angular resolution has been defined using the Al_2O_3 powder and was better than 0.1° in our angular range. The accuracy of temperature point setting was ± 2 K, the temperature point stability was ± 1 K. Heating and further cooling have been performed up to the 453 K temperature because it is known that the KNO_3 ferroelectric phase arises only if the sample cooling starts from the temperatures higher than $T = 443$ K [5,6]. The heating and cooling rates were 5 K/min.

3. Results and discussion

The measured diffraction spectra of the examined composites at several temperatures on cooling are shown in Fig. 1.

Peaks positions corresponding to the following crystal structures are marked: KNO_3 (dash lines), BaTiO_3 (dash-dot lines), Al_2O_3 substrate (arrows). Two structural phases of KNO_3 are marked by Greek symbols: β (393 K) and γ (ferroelectric phase, 383 K and below).

The splitting of some BaTiO_3 Bragg peaks as a result of PT into the ferroelectric phase has not been observed because of insufficient resolution. KNO_3 Bragg peaks used for identifying the α , β , γ phases are marked in Fig. 1. As the β - γ phase transition occurs the KNO_3 diffraction spectrum is modified as follows: the (012) β -phase peak at $2\theta \approx 26^\circ$ turns to the γ -phase (012) peak, while the shift is approximately 1° ; the (003) γ -phase peak arises at $2\theta \approx 29^\circ$; the β -phase (104) peak disappears at $2\theta \approx 42^\circ$. It is possible to conclude from the obtained diffraction data that the $\beta \rightarrow \gamma$ phase transition temperature is within the range of 383–393 K in both composites. It is in agreement with the value obtained from dielectric spectroscopy measurements ($\sim 397 \pm 2$ K). This temperature in pure KNO_3 is ≈ 397 K. After the γ - α phase transition the peaks (012) at $2\theta \approx 27^\circ$ and (110) at $2\theta \approx 32.5^\circ$ disappear; the following peaks arise: (111) and (021) at $2\theta \approx 23^\circ$, (112) at $2\theta \approx 34^\circ$, (221) and (041) at $2\theta \approx 42^\circ$.

The diffraction patterns of both composites at the same temperature $T = 363$ K on heating and cooling are shown in the Fig. 2. It is evident that there are peaks (111) and (021) corresponding to α -phase on heating but they are absent on cooling. The final temperatures in our measurements on cooling were 363 K for 0.75 $\text{KNO}_3 + 0.25 \text{ BaTiO}_3$ and 348 K for 0.5 $\text{KNO}_3 + 0.5 \text{ BaTiO}_3$ composites. From the obtained data it follows

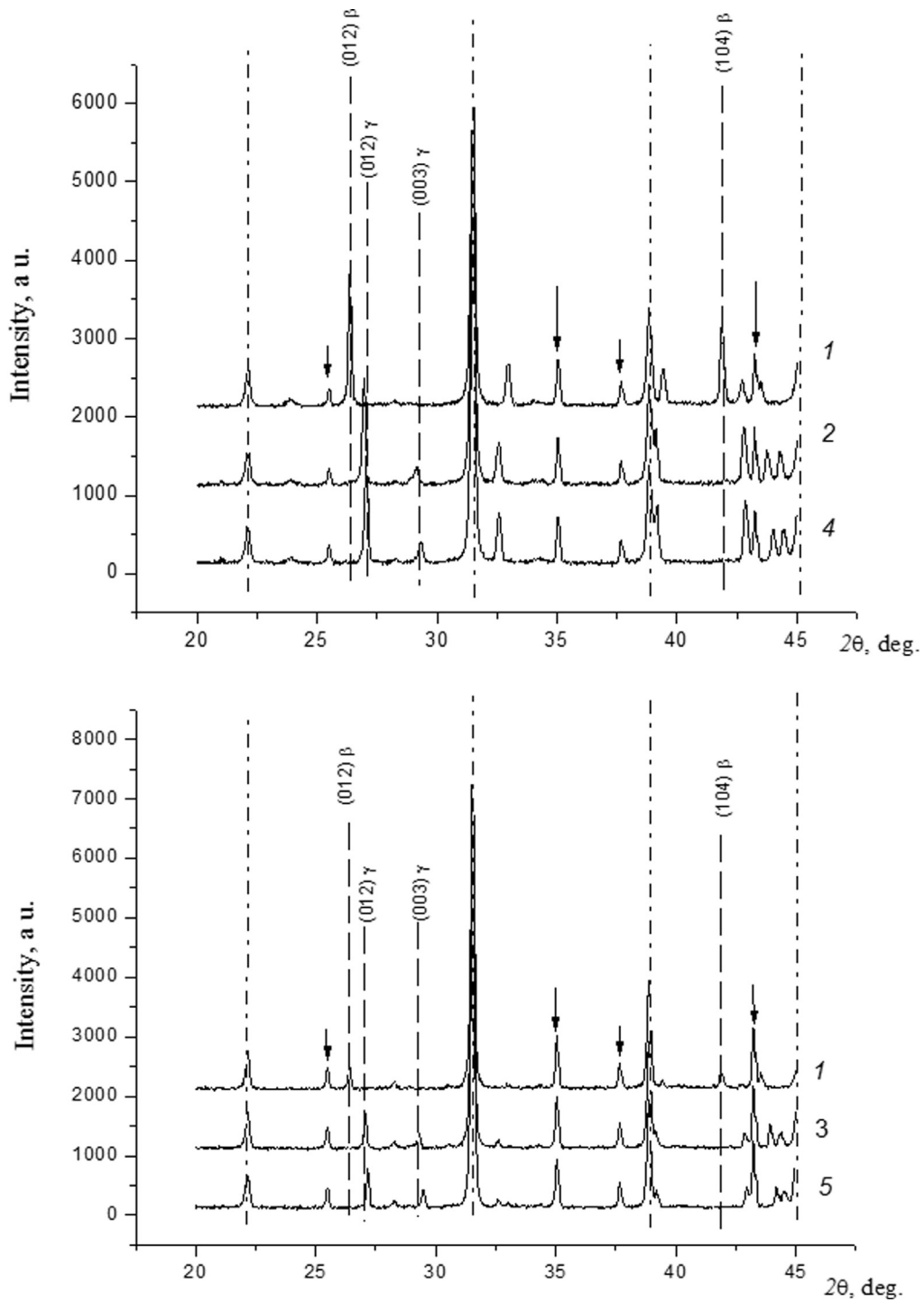


Fig. 1. The diffraction patterns of the $(1-x)\text{KNO}_3 + (x)\text{BaTiO}_3$ composites at (a) $x = 0.25$ and (b) $x = 0.5$ obtained on cooling at several temperatures T ; T (K): 393 (1), 383 (2), 373 (3), 363 (4), 348 (5).

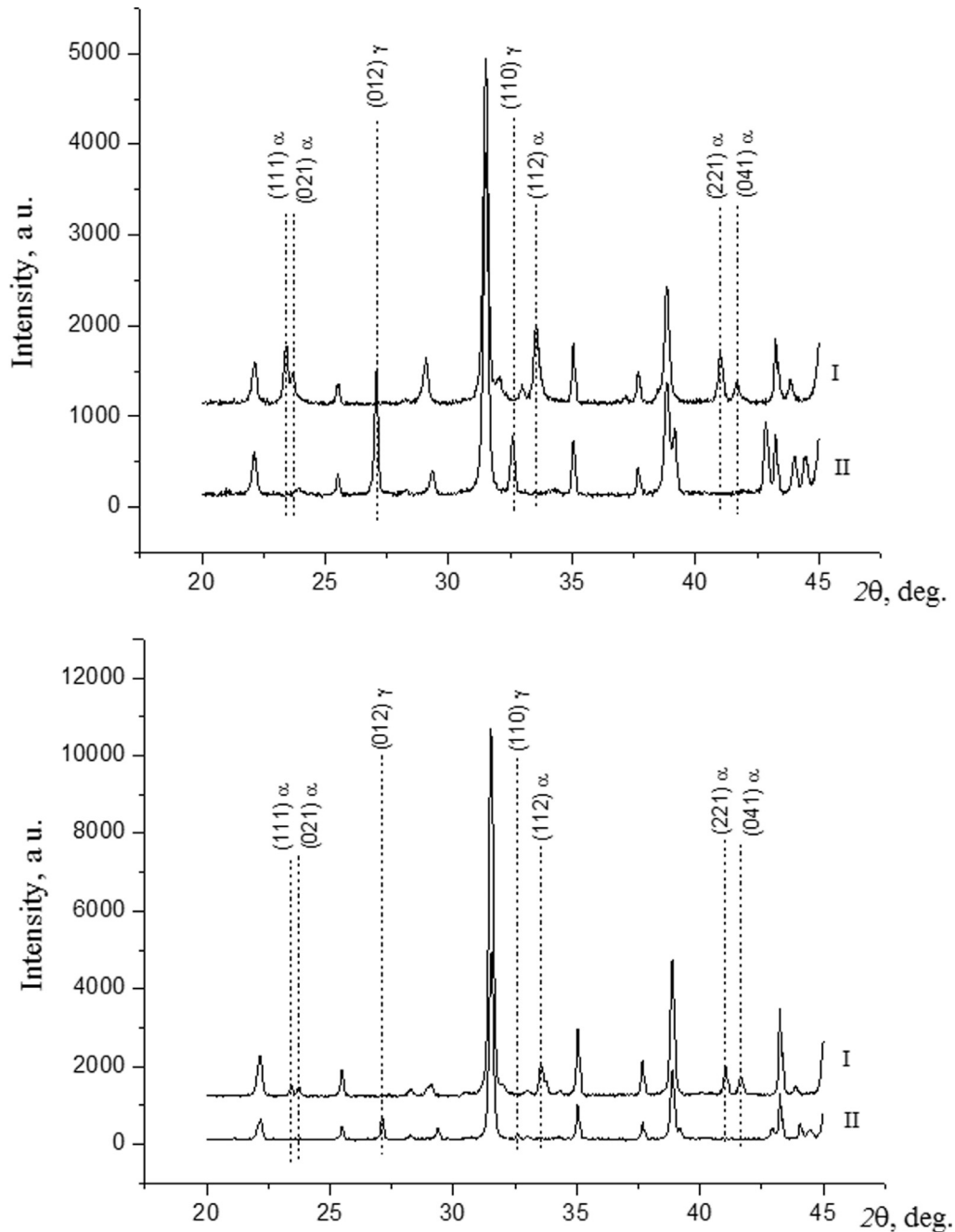


Fig. 2. Diffraction patterns of $(1-x)\text{KNO}_3 + (x)\text{BaTiO}_3$ at (a) $x = 0.25$ and (b) $x = 0.5$ obtained at the same temperature (363 K) on heating (I) and cooling (II). The positions of peaks used for KNO_3 phases identification are marked by dash lines.

that KNO_3 is in the ferroelectric state at these temperatures which are significantly lower than the γ - α transition temperature (≈ 378 K) in pure KNO_3 . This value can slightly (within several degrees) vary depending on the sample thermal history, cooling rate, humidity and so on [13].

It should be noted that the ferroelectric phase in KNO_3 has been observed at 348 K in the $(0.5)\text{KNO}_3 + (0.5)\text{BaTiO}_3$ composite (Fig. 3). The diffraction patterns for $(0.5)\text{KNO}_3 + (0.5)\text{BaTiO}_3$ calculated at this temperature (dash line) and experimental (solid line) are compared in Fig. 3. It is evident that these spectra differ

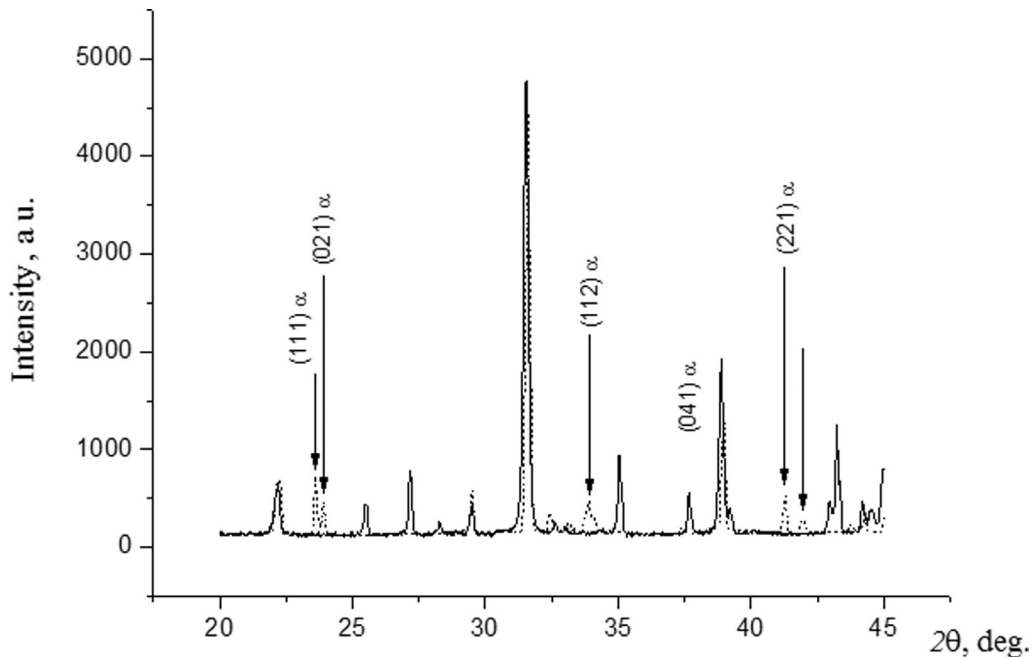


Fig. 3. Comparison of the model (dash line) and experimental (solid line) diffraction patterns of $(0.5)\text{KNO}_3 + (0.5)\text{BaTiO}_3$ at 348 K. The peaks corresponding to the α -phase are marked by arrows.

essentially: there are no peaks corresponding to the low-temperature paraelectric α -phase (marked by arrows), while the γ -phase peaks are visible on the experimental diffraction pattern (see Fig. 2 for comparison).

Thus the obtained results do not confirm the hypothesis about the suppression of the KNO_3 ferroelectric phase in the composite $(0.5)\text{KNO}_3 + (0.5)\text{BaTiO}_3$ at temperatures below 383 K [11,12]. A possible explanation for this disagreement is that the γ - α phase transition in KNO_3 has not happened yet at the lowest temperature (330 K) at which dielectric measurements have been performed in [11,12]. Indeed, linearly extrapolating the dependence of ΔT on BaTiO_3 particles concentration obtained in [9,10] out of the range $x = 0$ – 0.4 gives the value $\Delta T \sim 80$ K at $x = 0.5$. According to the dielectric data, the β - γ transition temperature practically does not depend on the BaTiO_3 concentration and is equal to $T_1 \sim 397 \pm 2$ K. So the γ - α PT should be expected below 320 K but the dielectric and structure measurements have not been performed in this temperature range. On the other hand, the ΔT vs x dependence may be nonlinear at the concentrations of $x > 0.4$ and the ferroelectric phase in KNO_3 may be stable down to the low temperatures in these composites with an increase in BaTiO_3 concentration. Further measurements at larger BaTiO_3 concentrations and at lower temperatures are necessary to clear up this situation. We are planning to conduct these studies in the nearest future.

The second reason of this disagreement may be a large broadening of the γ - α PT accompanied by a significant increase in transition time, as it has been observed in the KNO_3 and SiC powder mixtures [3].

4. Conclusion

The results of the structural studies have confirmed that the temperature interval of the KNO_3 ferroelectric phase in $(1-x)\text{KNO}_3 + (x)\text{BaTiO}_3$ composites increases significantly at $x = 0.25$. The KNO_3 ferroelectric phase becomes stable down to $T \sim 348$ K in the $(0.5)\text{KNO}_3 + (0.5)\text{BaTiO}_3$ composite. These results prove that the tendency of ferroelectric state stabilization remains with an increase in BaTiO_3 concentration above $x = 0.4$.

Acknowledgments

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