

Conference materials

UDC 537.226

DOI: <https://doi.org/10.18721/JPM.161.106>

Dielectric properties of ferroelectric composite $(\text{KNO}_3)_{3(1-x)}/(\text{RbNO}_3)_x$

A.Yu. Milinskiy ¹✉, S.V. Baryshnikov ¹, A.A. Zeeva ¹

¹ Blagoveshchensk State Pedagogical University, Blagoveshensk, Russia

✉ a.milinskiy@mail.ru

Abstract: The temperature dependences of the permittivity, the amplitude of the third harmonic and the differential thermal analysis signal for the $(\text{KNO}_3)_{3(1-x)}/(\text{RbNO}_3)_x$ composite were studied. To obtain $(\text{KNO}_3)_{3(1-x)}/(\text{RbNO}_3)_x$ samples, KNO_3 and RbNO_3 powders with particle size of 5–10 μm were used. The powders were mixed in appropriate proportions, after that the tablets were made at a pressure of $8 \cdot 10^3$ kg/cm². The samples with x from 0.05 to 0.5 were examined (x is the volume fraction of RbNO_3). Before measurements, the obtained samples were heated to 593 K, which is higher than the melting point of RbNO_3 , but lower than that of KNO_3 . It has been found that an increase in the RbNO_3 content leads to the appearance of additional phase transitions and the expansion of the temperature region of the ferroelectric phase. The transition temperatures for potassium nitrate do not shift along the temperature axis. For rubidium nitrate, the phase transition at 437 K decreases by 4–5 K, and the temperature hysteresis of this transition increases. The expansion of the ferroelectric phase upon cooling is explained by the superposition of the ferroelectric phases of potassium nitrate and the $\text{Rb}_x\text{K}_{(1-x)}\text{NO}_3$ solid solution.

Keywords: composite, ferroelectric, potassium nitrate, rubidium nitrate

Citation: Milinskiy A.Yu., Baryshnikov S.V., Zeeva A.A. Dielectric properties of ferroelectric composite $(\text{KNO}_3)_{3(1-x)}/(\text{RbNO}_3)_x$. St. Petersburg State Polytechnical University Journal: Physics and Mathematics. 16 (1.1) (2023) 49–53. DOI: <https://doi.org/10.18721/JPM.161.106>

This is an open access article under the CC BY-NC 4.0 license (<https://creativecommons.org/licenses/by-nc/4.0/>)

Материалы конференции

УДК 537.226

DOI: <https://doi.org/10.18721/JPM.161.106>

Диэлектрические свойства сегнетоэлектрических композитов $(\text{KNO}_3)_{3(1-x)}/(\text{RbNO}_3)_x$

А.Ю. Милинский ¹✉, С.В. Барышников ¹, А.А. Зеева ¹

¹ Благовещенский государственный педагогический университет, г. Благовещенск, Россия

✉ a.milinskiy@mail.ru

Аннотация. Исследованы температурные зависимости диэлектрической проницаемости, амплитуды третьей гармоники и сигнала ДТА для композита $(\text{KNO}_3)_{3(1-x)}/(\text{RbNO}_3)_x$. Установлено, что увеличение содержания RbNO_3 приводит к возникновению дополнительных фазовых переходов и расширению температурного интервала существования сегнетоэлектрической фазы.

Ключевые слова: композит, сегнетоэлектрик, нитрат калия, нитрат рубидия

Ссылка при цитировании: Милинский А.Ю., Барышников С.В., Зеева А.А. Диэлектрические свойства сегнетоэлектрических композитов $(\text{KNO}_3)_{3(1-x)}/(\text{RbNO}_3)_x$ // Научно-технические ведомости СПбГПУ: Физико-математические науки. 2023. Т. 16. № 1.1. С. 49–53. DOI: <https://doi.org/10.18721/JPM.161.106>

Статья открытого доступа, распространяемая по лицензии CC BY-NC 4.0 (<https://creativecommons.org/licenses/by-nc/4.0/>)



Introduction

Potassium nitrate is widely known as a material with a rectangular hysteresis loop, and it is a convenient material for creating a non-volatile ferroelectric memory [1]. However, the ferroelectric phase in KNO_3 appears only upon cooling in a narrow temperature range. A number of works reported attempts to expand the range of existence of the ferroelectric phase by creating composites and solid solutions, based on potassium nitrate [2–5]. For the ferroelectric composites $(\text{KNO}_3)_{(1-x)}/(\text{BaTiO}_3)_x$ [2] and $(\text{KNO}_3)_{(1-x)}/(\text{KNbO}_3)_x$ [3] an expansion of the region of existence of the ferroelectric phase of potassium nitrate is observed. It was reported about the expansion of the region of existence of KNO_3 ferroelectric phase in double salt systems of

$(\text{KNO}_3)_{(1-x)}/(\text{NaNO}_3)_x$ [4] and $(\text{KNO}_3)_{(1-x)}/(\text{AgNO}_3)_x$ [5]. As far as we know from publications, studies of potassium nitrate with other nitrate additives were not carried out. In this work, we study the effect of RbNO_3 on the formation of the ferroelectric state in KNO_3 .

Materials and Methods

Potassium nitrate at room temperature has an orthorhombic structure ($Pmcn$ space group) [6]. This phase is often referred to as phase II. When the sample is heated to about 401 K, a transition occurs to phase I, which has a disordered trigonal calcite-like structure $R3m$. Upon cooling, phase II does not directly transfer into phase I, but instead at $T = 397$ K it transfers into another trigonal phase III, which is ferroelectric with spontaneous polarization along the c axis. Spontaneous polarization is about $8\text{--}10 \mu\text{C}/\text{cm}^2$ at a temperature of 393 K. It was found that the temperature range of the existence of the ferroelectric state in KNO_3 depends on the thermal prehistory and cooling rate [7, 8] and upon preliminary heating of the sample to 473 K for the first heating-cooling cycle is about 22–24 K.

Rubidium nitrate has four stable forms. At room temperature, RbNO_3 has a trigonal space group $P3_1$ (phase IV) and crystallizes from an aqueous solution in the form of needles along the c axis [9]. This phase is stable up to 437 K and is pyroelectric with the formation of 180-degree pyroelectric domains. In the temperature range of 437–492 K rubidium nitrate exists in the cubic pyroelectric phase $Pm3m$ (phase III). According to [10], at the phase transition of 437 K the conductivity of RbNO_3 increases by two orders of magnitude, and this phase has superionic conductivity. In the range from 492 to 564 K [9] (or, according to [11], 558 K), RbNO_3 is in the rhombohedral phase $R3m$ (phase II). This phase is defined as antiferroelectric [12]. Above the phase transition at 564 K, RbNO_3 again transfers into a cubic phase $Fm3m$ (phase I), which exists up to the melting point of 587 K.

To obtain $(\text{KNO}_3)_{(1-x)}/(\text{RbNO}_3)_x$ samples, KNO_3 and RbNO_3 powders with a particle size of $5\text{--}10 \mu\text{m}$ were used. The powders were mixed in appropriate proportions, after which pellets with a diameter of 10 mm and a thickness of 1.5 mm were obtained by a pressure of $8 \cdot 10^3 \text{ kg}/\text{cm}^2$. Samples with x from 0.05 to 0.5 were used for the study (x is RbNO_3 volume fraction). The prepared samples were heated to a temperature of 593 K, which is higher than the melting point of RbNO_3 , but lower than that of KNO_3 . A photograph of the $(\text{KNO}_3)_{0.75}/(\text{RbNO}_3)_{0.25}$ sample surface is shown in Figure 1.

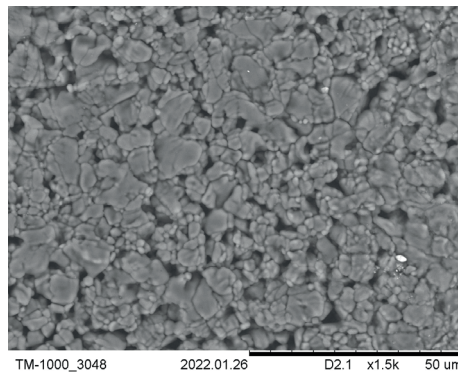


Fig. 1. Electron photograph of the $(\text{KNO}_3)_{0.75}/(\text{RbNO}_3)_{0.25}$ surface

To measure the dielectric permittivity of the samples, E7-25 digital immittance meter with a frequency range of 25–10⁶ Hz was used. In-Ga paste was used as electrodes. The measurements were carried out at a heating-cooling rate of ~ 1 K/min in the temperature range of 290–450 K. The temperature was recorded by a Center 340 electronic thermometer with a chromel-alumel thermocouple. The data was automatically recorded on a computer.

The setup for studying the nonlinear dielectric properties of the samples included a generator of harmonic oscillations with an operating frequency of 2 kHz. The electric field strength on the samples during the measurement was 50 V/mm. The signal was taken from a resistor connected in series with the sample and fed to a digital spectrum analyzer, which was a computer with analog to-digital converter ZET 230. To determine the region of existence of the ferroelectric phase we studied the coefficients of the third ($\gamma_{3\omega} = U_{3\omega}/U_{\omega}$) or fifth ($\gamma_{5\omega} = U_{5\omega}/U_{\omega}$) harmonics. The technique for studying ferroelectrics by using nonlinear dielectric spectroscopy is described in more detail in [13].

To study the samples by the method of differential thermal analysis (DTA), a Linseis STA PT 1600 synchronous thermal analyzer was used. The studies were carried out in the heating cooling mode at a rate of 1 K/min in the same temperature range as for dielectric measurements.

Results and Discussion

The temperature dependences of the permittivity $\epsilon'(T)$ and the third harmonic coefficient $\gamma_{3\omega}(T)$ for polycrystalline potassium nitrate are shown in Figure 2. If the sample is heated to 450 K, two anomalies are observed on the $\epsilon'(T)$ curve upon cooling. At $T = 397$ K, potassium nitrate transfers from phase I into a ferroelectric phase III, and at $T = 375$ K, a transition occurs from phase III to phase II, which is stable at room temperature. According to the data on the third harmonic coefficient $\gamma_{3\omega}(T)$ (see Fig. 1), the ferroelectric phase in potassium nitrate, which appears upon cooling, occupies a temperature range of approximately 22 K, which corresponds to the known data [6]. The third harmonic coefficient at its maximum is ~ 0.04 at $E = 50$ V/mm.

Figure 3 shows the temperature dependences of the permittivity $\epsilon'(T)$ and the third harmonic coefficient $\gamma_{3\omega}(T)$ for rubidium nitrate. As RbNO_3 is a pyroelectric, the third harmonic coefficient is ~ 0.01, however, it has a minimum at the phase transition, which is probably due to the vanishing of the pyroelectric polarization or a change of the piezoelectric coefficient.

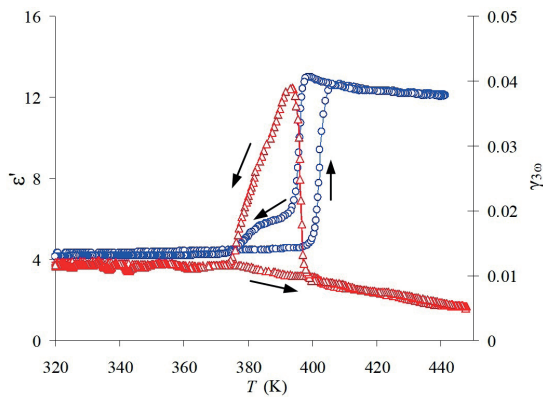


Fig. 2. Dependences $\epsilon'(T)$ at a frequency of 500 kHz (circles) and the coefficient of the third harmonic $\gamma_{3\omega}$ (triangles) for KNO_3 at a field strength of 50 V/mm

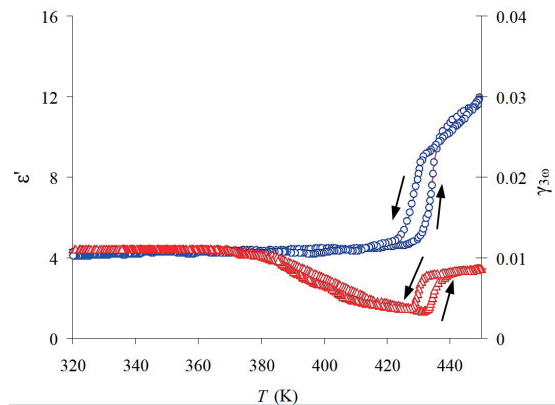


Fig. 3. Dependences $\epsilon'(T)$ at a frequency of 500 kHz (circles) and the third harmonic coefficient $\gamma_{3\omega}$ (triangles) for RbNO_3 at a field strength of 50 V/mm

For $(\text{KNO}_3)_{(1-x)}/(\text{RbNO}_3)_x$ composite samples, an increase in x is accompanied by an increase in the permittivity and expansion of the region of existence of the ferroelectric phase. The dielectric loss tangent in the ferroelectric phase at $T = 391$ K at a frequency of 20 kHz is: $\text{tg}\delta \approx 0.11$ for KNO_3 ; $\text{tg}\delta \approx 0.35$ for $x = 0.1$; $\text{tg}\delta \approx 0.6$ for $x = 0.3$; $\text{tg}\delta \approx 0.51$ for $x = 0.5$; and $\text{tg}\delta \approx 0.06$ for pure RbNO_3 . The range of existence of the ferroelectric state in $(\text{KNO}_3)_{(1-x)}/(\text{RbNO}_3)_x$ composite samples, determined from DTA diagrams, has a maximum at $x = 0.05$ (Fig. 4). In this case, as x increases, the amplitude of the third harmonic decreases (Fig. 5), which can be explained by a decrease in spontaneous polarization.

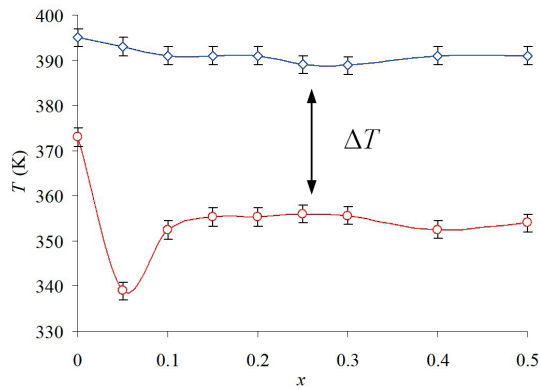


Fig. 4. Dependences of the temperature range of existence of the KNO_3 ferroelectric phase on the content of RbNO_3 in $(\text{KNO}_3)_{(1-x)}/(\text{RbNO}_3)_x$

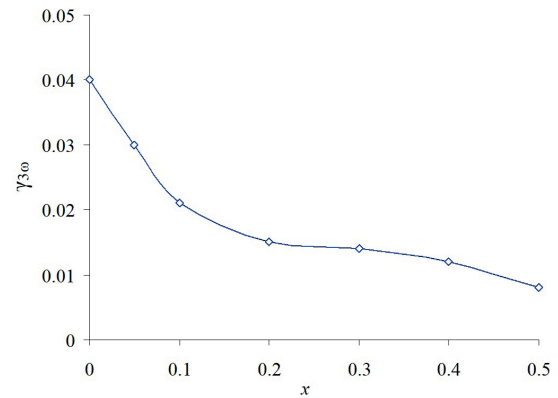


Fig. 5. Dependences of the amplitude $\gamma_{3\omega}$ on the content of rubidium nitrate in $(\text{KNO}_3)_{(1-x)}/(\text{RbNO}_3)_x$

To understand the results obtained, we compared them with the dielectric properties of $\text{K}_{(1-x)}\text{Rb}_x\text{NO}_3$ solid solutions, smelted from RbNO_3 and KNO_3 at a temperature of 530 K. Figure 6 shows the permittivities of the $(\text{KNO}_3)_{(1-x)}/(\text{RbNO}_3)_x$ composite and $\text{K}_{(1-x)}\text{Rb}_x\text{NO}_3$ solid solution for $x = 0.4$.

Analyzing the graphs, we can conclude that the $(\text{KNO}_3)_{0.6}/(\text{RbNO}_3)_{0.4}$ composite contains KNO_3 , RbNO_3 , and the $\text{RbK}_{(1-x)}\text{NO}_3$ solid solution, each having its own phase transition temperatures. In this case, the transition temperatures for potassium nitrate practically do not shift. For rubidium nitrate, the phase transition at $T = 437$ K decreases by 4–5 K, and the temperature hysteresis of this transition increases. The expansion of the ferroelectric phase upon cooling probably occurs due to the superposition of the ferroelectric phases of potassium nitrate and the $\text{K}_{(1-x)}\text{Rb}_x\text{NO}_3$ solid solution, which follows from the graphs, shown in Figures 6 and 7. The ferroelectric properties of $\text{K}_{(1-x)}\text{Rb}_x\text{NO}_3$ solid solution were studied in [14], where it was shown that the polar phase exists in the range of $x = 0$ to 0.56. In this case, P_s changes from 8.6 to 0.8 $\mu\text{C}/\text{cm}^2$. Hence, it follows that it is unlikely to obtain an interval of existence of a polar state greater than 40–55 K in the $(\text{KNO}_3)_{0.6}/(\text{RbNO}_3)_{0.4}$ composite.

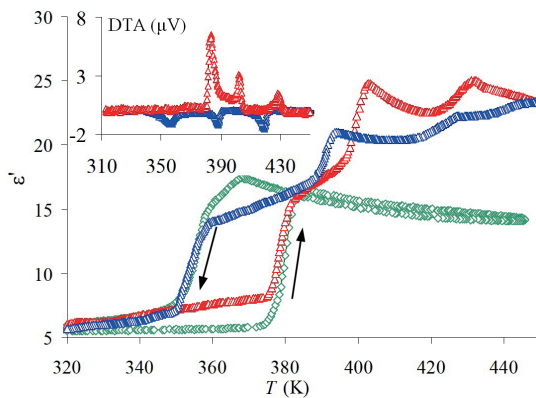


Fig. 6. Dependences $\varepsilon'(T)$ for the $(\text{KNO}_3)_{0.6}/(\text{RbNO}_3)_{0.4}$ composite (triangles) and $\text{RbK}_{(1-x)}\text{NO}_3$ solid solution (diamonds) at a frequency of 500 kHz. The inset shows the DTA signal for the same composite

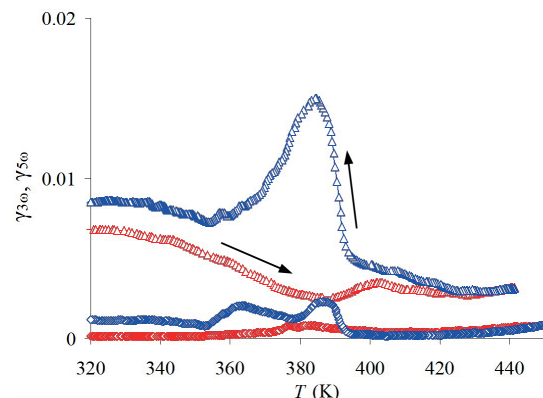


Fig. 7. Dependences $\gamma_{3\omega}(T)$ (triangles) and $\gamma_{5\omega}(T)$ (rhombuses) for $(\text{KNO}_3)_{0.6}/(\text{RbNO}_3)_{0.4}$ at a field strength of 50 V/mm

Conclusion

Thus, as shown by studies of $(\text{KNO}_3)_{(1-x)}/(\text{RbNO}_3)_x$ composites, the presence of RbNO_3 increases the temperature range of the ferroelectric state existence. The expansion of the polar state occurs due to the partial formation of the $\text{K}_{(1-x)}\text{Rb}_x\text{NO}_3$ solid solution, for which the temperature region of the polar phase is lower than that for pure KNO_3 .

REFERENCES

1. **Scott J.F.**, Ferroelectric Memories, Springer Series in Advanced Microelectronics. 2000.
2. **Stukova E.V., Baryshnikov S.V.**, Stabilization of the ferroelectric phase in $(\text{KNO}_3)_{1-x}(\text{BaTiO}_3)_x$ composites, Inorganic materials: applied research. 2 (2011) 434–438.
3. **Stukova E.V., Baryshnikov S.V.**, Expansion of the ferroelectric phase temperature interval in the composites $(\text{KNO}_3)_{1-x}(\text{BaTiO}_3)_x$ and $(\text{KNO}_3)_{1-x}(\text{PbTiO}_3)_x$, World Journal of Engineering. 3 (2010) 1055–1057.
4. **Shimada S., Aoki T.**, Stabilization of the ferroelectric γ -phase of KNO_3 by doping with Na^+ , determined by the acoustic emission method, Chemistry Letters. 25 (1996) 393–394.
5. **Rysiakiewicz-Pasek E., Antropova T., Polyakova I., Pshenko O., Cizman A.**, New insight into phase transitions of porous glass-based ferroelectric nanocomposites, Materials. 13 (2020) 3698.
6. **Chen A., Chernow A.**, Nature of Ferroelectricity in KNO_3 , Phys. Rev. 154 (1967) 493–505.
7. **Deshpande V.V., Karkhanavala M.D., Rao U.R.K.**, Phase transitions in potassium nitrate, J. of Therm. Anal. and Cal. 6 (1974) 613–621.
8. **Nimmo J.K., Lucas B.W.**, The crystal structures of γ - and β - KNO_3 and the $\alpha \leftarrow \gamma \leftarrow \beta$ phase transformations, Acta Cryst. B32 (1976) 1968–1971.
9. **Bury P.C., McLaren A.C.**, Pyroelectric Properties of Rubidium, Cesium, and Thallium Nitrates, Phys. Stat. Sol. 31 (1969) 799–806.
10. **Salhotra P.P., Subbarao A.C., Venkateswarlu P.**, Polymorphism of Rubidium Nitrate, Phys. Stat. Sol. 31 (1968) 859–854.
11. **Fujimoto S., Yasuda N., Shimizu H., Tsuboi S., Kawabe K., Takagi Y., Midorikawa M.**, Dielectric properties of rubidium nitrate under hydrostatic pressure, J. Phys. Soc. Jpn. 42 (1977) 911–915.
12. **Yamamoto S., Suematsu Y., Shinnaka Y.**, X-Ray study of phase transition in RbNO_3 , J. Phys. Soc. Jpn. 7 (1977) 1962–1967.
13. **Ikeda S., Kominami H., Koyama K., Wada Y.**, Nonlinear dielectric constant and ferroelectric-to-paraelectric phase transition in copolymers of vinylidene fluoride and trifluoroethylene, J. Appl. Phys. 62 (1987) 3339–3342.
14. **Kawabe U., Yanagi T., Sawada S.**, Dielectric and X-ray studies of KNO_3 -series mixed crystal, J. Phys. Soc. Japan 20 (1965) 2059–2073.

THE AUTHORS

MILINSKIY Alexey Yu.
a.milinskiy@mail.ru
ORCID: 0000-0001-7525-4396

ZEEVA Anna A.
anutka_2010.1997@mail.ru
ORCID: 0000-0001-7216-3931

BARYSHNIKOV Sergey V.
svbar2003@list.ru
ORCID: 0000-0002-3362-8975

Received 01.10.2022. Approved after reviewing 22.11.2022. Accepted 23.11.2022.