



Dielectric properties of a potassium nitrate–ammonium nitrate system

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Abstract

Potassium nitrate has a rectangular hysteresis loop and is thought to be a promising material for non-volatile ferroelectric memory. However, its polar phase is observed in a narrow temperature range. This paper deals with an effect of ammonium nitrate NH_4NO_3 on the dielectric properties of potassium nitrate. Thermal dependencies of the linear dielectric permittivity ε and the third-harmonic coefficient g_3 for potassium nitrate and polycrystalline binary $(\text{KNO}_3)_{1-x}(\text{NH}_4\text{NO}_3)_x$ system ($x = 0.025, 0.035, 0.050, 0.100$) in the temperature range between 300 and 460 K have been investigated. A temperature range extension of the ferroelectric phase with increasing the x value was revealed. The ferroelectric phase was retained in the $(\text{KNO}_3)_{1-x}(\text{NH}_4\text{NO}_3)_x$ composites ($x = 0.050, 0.100$) down to room temperature. A thermodynamic model for the ammonium-nitrate effect on the temperature of reconstructive phase transition $\text{II} \rightarrow \text{I}$ in potassium nitrate was suggested.

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1. Introduction

Potassium nitrate KNO_3 shows much promise as a material that could be used in creating non-volatile memory [1]. The ferroelectric phase in this compound appears only at cooling and in a narrow temperature range. Studies [2–10] examined the influence of various factors on the size of the temperature range of the ferroelectric phase in potassium nitrate. For example, the influence of Na^+ and Rb^+ ions on the ferroelectric properties of KNO_3 was studied [2,3]. A large number of works were dedicated to studying various size

effects in potassium nitrate [4–9]. Confined geometry was observed to influence the formation of the KNO_3 ferroelectric phase in thin films [4], porous glasses [5, 6] and MCM-41 matrices [7–9]. A study of KNO_3 in porous glasses by differential scanning calorimetry in [5] revealed a widening in the range of the ferroelectric phase III from 15K in a bulk sample to temperatures about 20 and 37K in samples with particle sizes of 160 and 23 nm, respectively. Recently, there have been studies of the ferroelectric state in potassium nitrate and perovskite-like ferroelectric-based composites [10]. Significantly, all of the above-mentioned works reported a widening of the region where the ferroelectric phase existed relative to that of pure potassium nitrate.

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The present work is dedicated to studying linear and non-linear dielectric properties of the $(\text{KNO}_3)_{1-x}(\text{NH}_4\text{NO}_3)_x$ ($x = 0,025, 0,035, 0,050, 0,100$) polycrystalline binary system in the temperature range of 300–460 K compared to the similar properties of pure potassium nitrate.

2. Samples and experimental procedure

Potassium nitrate at room temperature and ambient pressure has an orthorhombic structure and a space group $Pm\bar{c}n$ (phase II) [11]. When a sample is heated to 401 K, there occurs a phase transition to phase I with a disordered trigonal calcite-like $R\bar{3}m$ structure. At cooling a transition from a high-temperature phase I to phase III with a spatial symmetry $R3m$ may be observed at 397 K. At lower temperatures there is a transition from phase III to phase II that is stable at room temperature. Phase III is ferroelectric and is observed only when a sample is cooled after previously having been heated to a temperature no lower than 453 K. Transitions between phases II and I or III are reconstructive, i.e., their symmetries do not obey the group-subgroup relation. Potassium nitrate is an improper ferroelectric. In phase III it exhibits spontaneous polarization aligned along the c axis. At a temperature of 390 K, the absolute value of the polarization vector $P_s = 8-10 \mu\text{C}/\text{cm}^2$ [11]. It has been found that the temperature range where the ferroelectric state in KNO_3 exists depends on the thermal history and the cooling rate [12,13], and for samples that have been pre-heated to 470 K this range for the first heating-cooling cycle is about 24 K.

Ammonium nitrate may be in five different phases in the studied temperature range [14]. An orthorhombic phase with a space group $Pm\bar{m}n$ is stable in the range from room temperature to 305 K. The orthorhombic structure possesses a space group $Pnma$ in the temperature range of 305–357 K. Upon further heating from 357–443 K, a tetragonal phase with a space group $P421m$ is stable. For temperatures above 443 K ammonium nitrate has a cubic structure and a space group $Pm\bar{3}m$.

The phase composition of the potassium-ammonium nitrate mixture was studied in [15,16]. Solid solutions of ammonium nitrate dissolved in potassium nitrate form only for temperatures lower than 298 K. For higher temperatures, there is a larger amount of another phase that is a solid solution of ammonium nitrate in a metastable phase III potassium nitrate. According to the data in [15,16], a mixture of potassium and ammonium nitrates in the studied concentrations forms solid solutions with the crystalline structure of potassium nitrate preserved. Ammonium nitrate is incorporated into the KNO_3

crystalline lattice. We may assume that an admixture of small quantities of ammonium nitrate must induce local distortions causing a change of dielectric properties and a shift in phase transitions in potassium nitrate crystals. The dielectric properties of the $\text{KNO}_3\text{--NH}_4\text{NO}_3$ systems have not, to the best of our knowledge, been previously studied.

Samples of the $(\text{KNO}_3)_{1-x}(\text{NH}_4\text{NO}_3)_x$ ($x = 0.025, 0.035, 0.050, 0.100$) crystalline binary compounds were prepared by evaporation from an aqueous solution: the basic substances in the necessary amounts were carefully stirred in distilled water, and the obtained mixture was evaporated at 400–405 K. Polycrystalline samples in the form of tablets that were 1 cm in diameter and 1.2 mm thick were pressed from the obtained powders at pressures of 600–700 MPa. Polycrystalline KNO_3 samples of the same sizes were used for comparison.

A digital E7-25 LCR meter at a frequency of 1 MHz was used to measure the dielectric permittivity. Indium-gallium paste was used to make electrodes. Measurements were taken for heating and cooling rates of about 2 K/min, in a temperature range covering the KNO_3 phase transitions. The temperature was recorded with an electronic Center 340 thermometer with a chromel-alumel thermocouple. Temperature stabilization was no worse than 0.2 K. Samples were heated for 30 min at 380 K to remove the adsorbed water. The error of determining the permittivity and the third-harmonic coefficient was no higher than 5%.

The setup for temperature studies of higher harmonics included a sinusoidal generator with an operational frequency of 2 kHz. The signal was taken from a resistor that was series-connected with the sample and then fed into a computer with a 24-bit analog-to-digital ZET 230 converter and ZetLab software serving as a spectral analyzer.

For high electric fields the relationship between polarization and an electric field is described by a power series in powers of E :

$$P = \varepsilon_0(\varepsilon_1 E + \varepsilon_2 E^2 + \varepsilon_3 E^3 + \varepsilon_4 E^4 + \varepsilon_5 E^5 + \dots), \quad (1)$$

where the ε_1 coefficient is the linear permittivity, and ε_i are the i th-order permittivities.

In the case of ferroelectric materials, non-linear terms must not be neglected even in relatively low electric fields.

As a result of the non-linear dependence (1), when an electric field varying by the law $E = E_0 \cos(\omega t)$ is applied to the sample, higher harmonics with frequencies $2\omega, 3\omega, \dots$ whose amplitudes are determined by the values $\varepsilon_2, \varepsilon_3,$

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