Dielectric response of potassium nitrate in a restricted geometry

E. Koroleva [a, b, *], A. Naberezhnov [a, b], E. Rysiakiewicz-Pasek [c], S. Vakhrushev [a, b], A. Sysoeva [a], Yu. Kumzerov [a]

[a] Ioffe Institute, Polytekhnicheskaya 26, 194021, St.-Petersburg, Russia
[b] Peter the Great St. Petersburg Polytechnic University, Polytekhnicheskaya 29, 195251, St.-Petersburg, Russia
[c] Institute of Physics, Wrocław University of Technology, W. Wyspiańskiego 27, 50-370 Wrocław, Poland

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ABSTRACT

The dielectric properties of nanocomposite materials (NCM) on basis of porous glasses with KNO_3 embedded into the pores have been studied in the temperature interval 293 K–570 K and in the frequency diapason $0.1-10^7$ Hz. The three types of porous glasses with average pore diameter 320 (PG320), 46 (PG46) and 7 (PG7) nm have been used for production NCM from melted KNO_3. It is shown that dielectric permittivity demonstrates the essential growth in the high-temperature phase for all types of NCM. The temperature of the ferroelectric phase transition decreases at a reduction of average pore diameters and the temperature interval of stability of ferroelectric phase essentially enlarges. In case of NCM on basis of PG7 there is no any anomalies corresponding to the phase transition in this NCM and on cooling up to room temperature ferroelectric phase remains stable. From analysis of dielectric response, the relaxation process responsible for the ferroelectric phase transition has been detected and the temperature dependencies of process parameters have been determined.

1. Introduction

The studies of ferroelectrics in a restricted geometry especially embedded into artificial and natural porous media (so-called nanocomposite materials − NCM) have shown that these materials have demonstrated a row of unique properties such as the giant dielectric permittivity in the high-temperature paraelectric phase [1–5], the crossover of the ferroelectric phase transition (PT) from discontinuous to continuous type as a function of ferroelectric nanoparticles sizes [6,7], the formation of "pre-melted" state above Curie temperature T_C accompanying by sharp increasing of ion mobilities [8,9] and etc. In particular, the dielectric measurements of $NaNO_2$ [1,2,10], KH_2PO_4 (KDP) [2,11], KD_2PO_4 (DKDP) [5], Roshelle salt [2], KNO_3 [3,4] within porous glasses and artificial opals have shown the unexpected growth of the real and imaginary parts of the dielectric susceptibility ε above the temperature T_C of the ferroelectric PT and the shift of this PT temperature.

At ambient conditions potassium nitrate exists in different modifications depending on temperature. The low-temperature orthorhombic α-phase transforms upon heating into the trigonal disordered β-phase at ~400 K. This phase remains stable up to the melting at ~606 K. Upon cooling an intermediate ferroelectric phase with the trigonal symmetry (γ-phase) appears in a vicinity of T_C ~ 393 K and transforms into α-phase below ~378 K [12,13]. The stability of this γ-phase depends on the thermal pre-history and the cooling rate [14]. It is shown [15] that for the thin films of KNO_3 the γ-phase exists essentially below the room temperature. This fact opens a possibility to use the thin KNO_3 films as materials for production nonvolatile ferroelectric random access memory (FeRAM) [16]. In Ref. [17] the authors have demonstrated that such films have address voltages between 2 and 6 V, depending on the thickness, and switching times as fast as 20 ns. In spite of these very promising results (from possible application point of view) many questions remain open. Up-to-now it is unknown whether the γ-phase is really stable at low temperature or it is a metastable phase and exists because of presence of elastic strains or may be due to size effect. The question why the temperature range of stability of the ferroelectric phase for thin films is wider than for the bulk has no unequivocal answer.

Utilization of various porous media with different average pore sizes give a possibility to study the influences of size effect and interface on properties of NCM with KNO_3 embedded into the pores. The recent reports [3,4,18,19] carrying out for NCM on base of MCM-41 and porous glasses with average pore diameters 320 and 46 nm have shown that the decreasing of pore diameters results in

broadening of temperature range where γ-phase is stable. The principle goal of this contribution was to study the dielectric properties of NCM on base of porous glasses with average pore diameters 320, 46 and 7 nm filled by KNO_3 in the wide frequency range $0.1-10^7$ Hz, to identify the relaxation processes taking place in a restricted geometry, to obtain their temperature dependences and the information concerning to PT in these NCM.

2. Samples and experiment

Porous glasses were obtained by an etching of sodium borosilicate glass after phase separation procedure. Rectangular glass plates of the size of $10 \times 10 \times 0.5$ mm^3 were cut out from the original glass. The obtained porous glasses contained about 90% of SiO_2. The average pore diameters were determined by the adsorption poroscopy and the mercury porosimetry and were 320 ± 20 nm for PG320, 46 ± 6 nm for PG46 and 7 ± 2 nm for PG7. The porosities determined by the mass decrement after leaching were 45% (PG320), 50% (PG46) and 23% (PG7). All samples were filled by melted KNO_3. The dielectric response was studied at the frequencies 0.1 $Hz-10$ MHz and the temperature diapason $293-570$ K using Novocontrol BDS80. At measurements we have used the thin gold electrodes. Possible remnant water into the pores was removed by drying at 380 K in the nitrogen atmosphere.

3. Results and discussion

The temperature dependences of complex dielectric permittivity (ε' and ε'') of three types NCM (PG320 + KNO_3, PG46 + KNO_3 and PG7 + KNO_3) at different frequencies upon heating and cooling are presented in Fig. 1, Fig. 2 and Fig. 3. Unlike massive potassium nitrate the exponential growth of ε for all nanocomposites is observed at heating. The growth of ε is more noticeable at low measuring frequencies. It is necessary to note that the value of ε is essentially higher than in the bulk and grows with decreasing of pore diameter of porous matrix. For example at 380 K and at 12 Hz real part of dielectric permittivity ε' for PG320 + KNO_3 is higher by an order of magnitude than ε' for the bulk KNO_3, and in turn ε' for PG7 + KNO_3 is higher by an order of magnitude than ε' for PG320 + KNO_3. The real part of dielectric permittivity ε' for PG7 + KNO_3 at 550 K and at 12 Hz reaches 10^7. For all NCM the frequency dispersion is observed in all studied temperature range. The similar behavior of ε' is observed also for other ferroelectric materials — sodium nitrite, KDP, Rochelle salt [1,2,5,20] embedded into porous matrixes and originates due to non-uniform conductivity of these composites [21].

Let's consider the behavior of ε near the phase transitions for different NCM. The temperatures of phase transitions in the bulk KNO_3 point out by the vertical dashed lines in Figs. 1—3 for clearness. Upon heating NCM PG320 + KNO_3 (Fig. 1) the jump of ε is observed in a vicinity 403 K and corresponds to the first-order PT from the paraelectric α-phase to the paraelectric β-phase. This PT temperature is very close to the temperature of α → β PT for the bulk KNO_3 (403 K). Upon cooling we have not observed the anomaly corresponded to β → γ PT. So we don't observe the pronounced jump in the dependence ε (T). PT from γ-phase into α-phase occurs more sharply and we have observed a sharp step in the dependence ε (T) near 375 K. This temperature corresponds to γ → α PT in the bulk KNO_3. Decreasing of average pore diameter (and characteristic sizes of potassium nitrate clusters according to diffraction data [10,22,23]) leads to further smearing of PT and shifting of T_C to lower temperatures. Our neutron and X-rays diffraction studies [10,22,23] have shown that PT to the ferroelectrics state occurs gradually and in PG46 + KNO_3 the coexistence of α, γ and β phases takes place in a wide temperature range 320—380 K. In this NCM (Fig. 2) upon
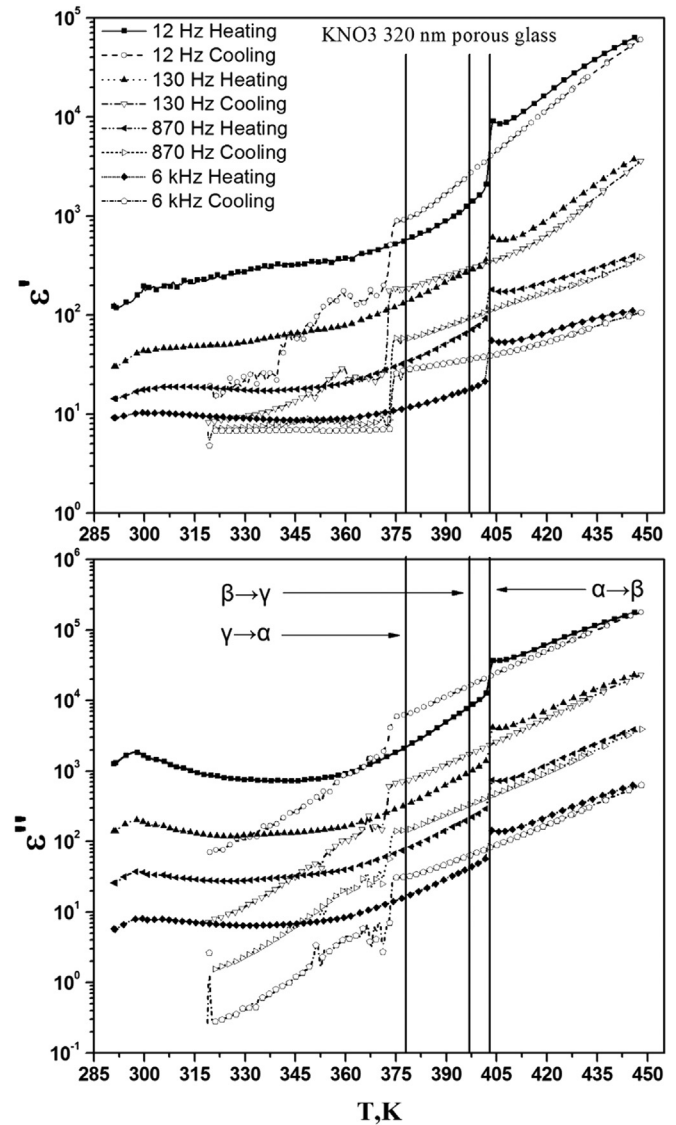

Fig. 1. Temperature dependences of real and imaginary parts of dielectric permittivity of KNO_3 within PG320 on heating and cooling at indicated frequencies. Vertical dashed lines point out the temperatures of α → β, β → γ, γ → α transitions for the bulk KNO_3.

heating the temperature of α → β PT shifts to higher temperatures and we observe a more diffuse step on temperature dependence in a vicinity 410 K. At cooling we see only a change of slope in ε (T) near 375 K. The diffraction studies point out that in the temperature range 375—340 K on cooling the fraction of γ-phase increases up to ~80% (from total amount of the embedded salt) at 340 K, the fraction of β-phase decreases and disappears practically below 340 K and the α-phase arises at 375 K and achieves ~20% at 340 K. This ratio of α/γ phases remains practically stable at cooling down to room temperature. Essentially more interesting situation is observed in PG7 + KNO_3 (Fig. 3). On temperature dependence ε' there is a very pronounced bend near 530 K. Its appearance is caused by the beginning of melting of potassium nitrate nanoparticles. It is necessary to note that this temperature is lower on 70° than T_{melt} (~606 K) of the bulk KNO_3. Above ~575 K KNO_3 embedded into PG7 exists in the melting state. There is a hysteresis (~35 K) between the heating and cooling curves. As for structural phase transitions we see a small anomaly around 420 K upon heating and a frequency-dependent anomaly in the temperature area of coexistence β- and γ-phases upon cooling. Our diffraction studies point out that on cooling down