Electrocaloric and Pyroelectric properties of ferroelectric nanoparticles with size distributed according to the truncated Normal distribution

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Introduction

For many years, pyroelectric (PE) converters have been used in many applications from gas detectors to thermal imaging, however, only the recently discovered "giant" electrocaloric (EC) effect in thin films opened up the prospect for using the EC effect in solid-state microcoolers. The EC and PE properties of nanoscale materials are very different from those of bulk materials. Therefore, studies of low-dimensional FE materials, are very relevant.

There are a number of technological and theoretical difficulties in research of ferroelectric (FE) nanocomposites (NCs). Modern methods allow precise selection of nanoparticles (NP) by size and shape, however, NCS made on their basis, as a rule, contain NPs with a more/less symmetric distribution in size within certain limits around the average.

In this case, the properties of the composite depend on the predominance of the contribution of particles of one size or another. The numerical and analytical models developed to date are mainly aimed at the description of composites with nanoparticles of the same size and certain shape.

The **aim** of the work is to calculate and analyze the influence of the NPs size distribution function parameters on the polar, EC and PE properties of the ensemble, and corresponding hysteresis loops. For practical applications the dependence of PE figures of merit on the average NPs size for different parameters of the distribution function was calculated and briefly analyzed.

Landau-Ginzburg-Devonshire (**LGD**) theory and truncated normal distribution were used to achieve this aim.

Object of study

Let us consider an ensemble of non-interacting spherical ferroelectric nanoparticles (R_i, ε_b) placed in a dielectric medium (ε_e) and covered with a semiconducting shell (Λ, ε_{IF}), which screening the ferroelectric polarization of the particle [Fig. 1]. The nanoparticles are characterized by a distribution function $f(R)$.

The nanoparticles in a ferroelectric phase have a one-component spontaneous polarization $P_3(r)$ directed along the crystallographic axis 3 (so-called, single-domain state).

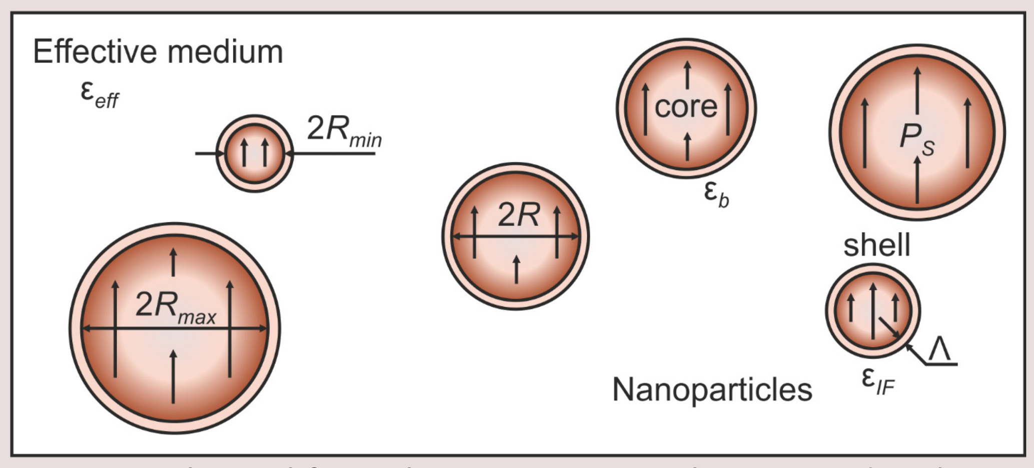

Fig 1. Spherical ferroelectric nanoparticles covered with a semiconducting shell and placed in dielectric medium

Analytical Dependences

Using phenomenological Landau-Ginsburg-Devonshire (LGD) theory and effective medium approximation, earlier [1] we calculated analytically typical dependences of the PE and EC conversion parameters on the external electric field, temperature, and radius of spherical single-domain FE nanoparticles with fixed radius.

At that, the contribution of strains and polarization gradients, as well as the depolarization and screening effects should be taken into consideration by introducing an appropriate factor (1).

$$\eta(R,\Lambda)=3\varepsilon_e/\left[\varepsilon_b+2\varepsilon_e+\varepsilon_{IF}(R/\Lambda)\right] \qquad (1)$$

Polarization corresponds to the equation (2). The dynamic relative dielectric permittivity defined by (3) corresponds to the equation (4).

$$\Gamma\frac{\partial P}{\partial t}+\alpha_T(T-T_{cr})P+\beta P^3+\gamma P^5=\eta E_{ext} \qquad (2)$$

$$\varepsilon_{33}=1+\frac{1}{\varepsilon_0}\frac{\partial P}{\partial E_{ext}} \qquad (3)$$

$$\Gamma\frac{\partial\chi_{33}}{\partial t}+\left[\alpha_T(T-T_{cr}(R,\Lambda))+3\beta P^2+5\gamma P^4\right]\chi_{33}=\eta \qquad (4)$$

The numerical calculations were done for the case when $f(R)$ is a truncated normal Gaussian distribution (8). Since the radii are distributed between R_{min} and R_{max} the distribution function is normalized as (9) with coefficient (10).

Since the nanoparticle sizes are distributed, all composite parameters should be averaged using the distribution function (8), where F_{NP}(R) is parameters of single NP.

$$f(R)=\begin{cases}1/\sigma_R\exp\left[-(R-R_m)^2/(2\sigma^2)\right]; & R\in[R_{min};R_{max}];\\ 0; & R\in(-\infty;R_{min})\cup(R_{max};+\infty),\end{cases} \qquad (5)$$

$$\int_{R_{min}}^{R_{max}} f(R)\,dR=1 \qquad (6)$$

$$\sigma_R=\sqrt{\frac{\pi}{2}}\sigma\left[\mathrm{erf}\left(\frac{R_m-R_{\min}}{\sqrt{2}\sigma}\right)-\mathrm{erf}\left(\frac{R_m-R_{max}}{\sqrt{2}\sigma}\right)\right] \qquad (7)$$

$$F_{ensemble}=\int_{R_{min}}^{R_{max}} F_{NP}(R)\cdot f(R)\,dR \qquad (8)$$

PE and EC coefficient defined by (9) and (10).

$$\Pi(R,\Lambda)=\frac{\alpha_T P+\beta_T P^3+\gamma_T P^5}{\alpha_T\left[T-T_{cr}(R,\Lambda)\right]+3\beta P^2+5\gamma P^4} \qquad (9)$$

$$\Sigma=d\Delta T_{EC}/dE_{ext} \qquad (10)$$

In [1], the Figure of Merit were considered in the form:

$$F_I=\Pi/c_{NP},\ F_f=\Pi/(\varepsilon_0\varepsilon_{NP}),\ F_{EQ}=\Pi^2/(\varepsilon_0\varepsilon_{NP}),$$
$$K_{PE}=\Pi^2/(\varepsilon_0\varepsilon_{NP}c_{NP}),\ F_{EU}=\Pi^2/\left(\varepsilon_0\varepsilon_{NP}c_{NP}^2\right)$$

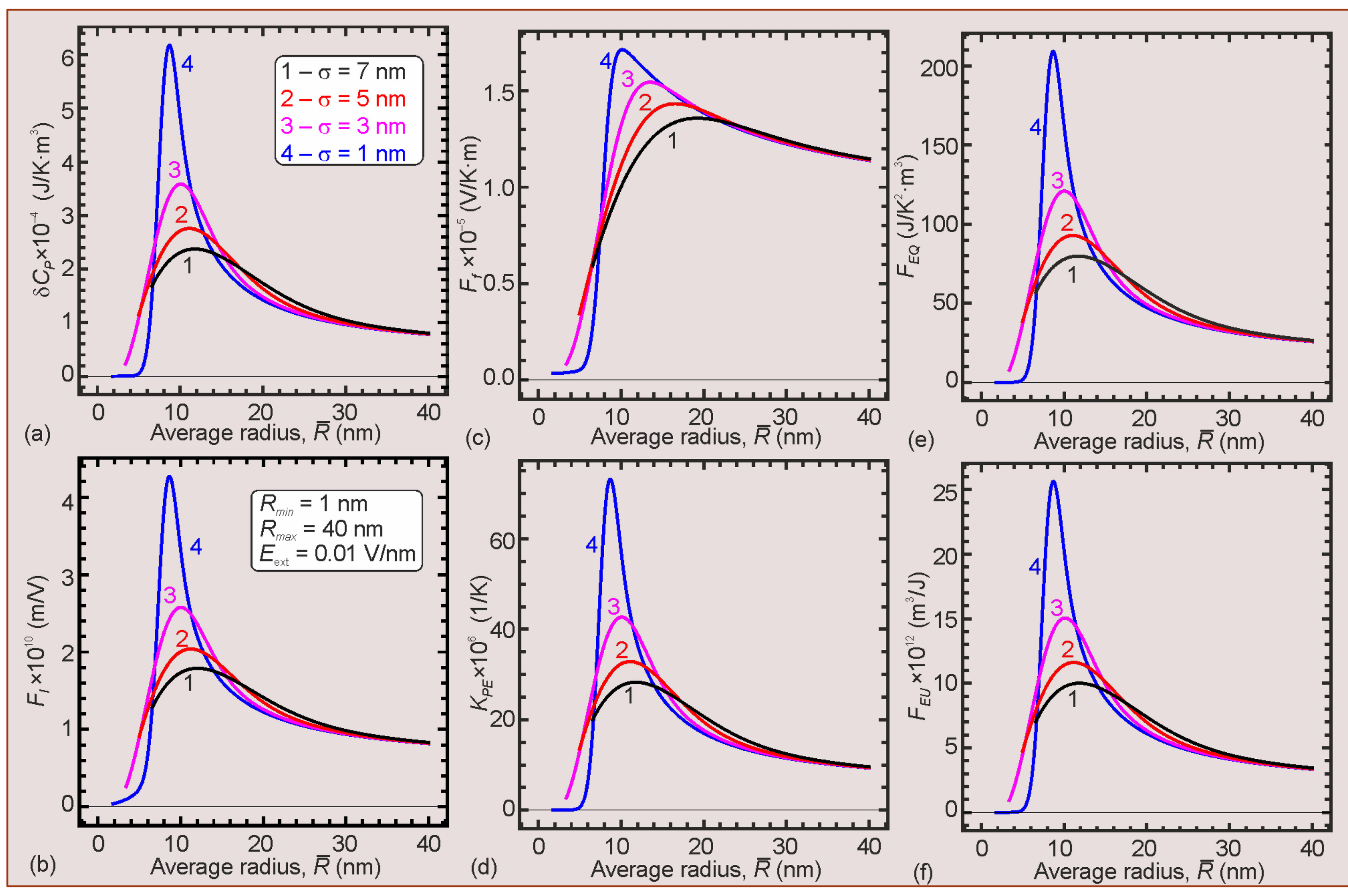

Fig 2. Dependences of specific heat variation $\delta C_P\equiv C_P-C^0_P$ (a), and PE performances F_I (b), F_f (c), K_{PE} (d), F_{EQ} (e) and F_{EU} (f) on the ***average radius*** $\bar{R}$ of $BaTiO_3$ nanoparticles (curves 1-4) in the ensemble, calculated for different σ = 7, 5, 3, 1 nm, E_{ext} = 0.01 V/nm, and R_{max} = 40 nm

We calculated and analyzed the dependences of the FoM on $\bar{R}$. The characteristics indicate the presence of a phase transition induced by a change in particle size, which is characterized by the presence of a maxima near the critical radius. The value of this radius increases [in the range of 8 nm – 12 nm] with an increase in the standard deviation [in the range of 1 nm – 7 nm]. More details of FoM calculations can be found in [2]

Results, discussion and conclusions

$$\bar{R}(R_m)=\int_{R_{min}}^{R_{max}} R\cdot f(R)\,dR=\frac{\sigma^2}{\sigma_R}\left(\exp\left[-\left(\frac{R_m-R_{min}}{\sqrt{2}\sigma}\right)^2\right]-\exp\left[-\left(\frac{R_m-R_{max}}{\sqrt{2}\sigma}\right)^2\right]\right)+R_m$$

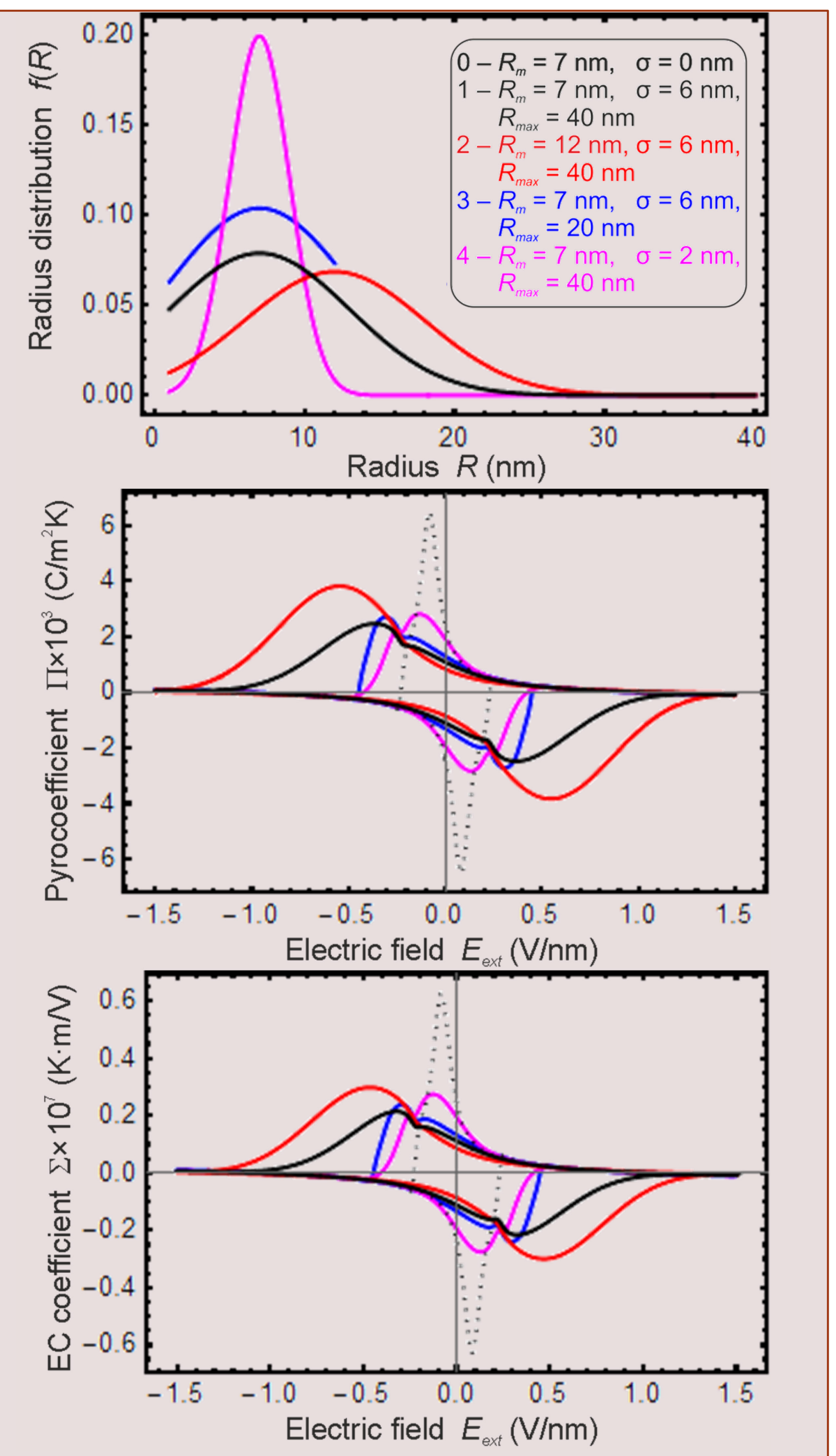

Fig 1. Dependences of the PE (b) and EC (c) coefficients on an external electric field calculated for an ensemble of noninteracting BaTiO3 nanoparticles (curves 1-4), which radii are distributed in accordance with (a)

Some of the Π and Σ loops are characterized by the presence of two positive and two negative maxima corresponding to positive and negative electric field. The shape of the loop for σ = 2 nm is significantly different from the shape of the loops. A decrease in σ corresponds to a decrease in the height of one maximum, its "splitting" into 2 maxima, and then to an increase in the height of the other maximum. Note the shift of the maxima towards higher fields with R_m (or σ) increase.

In conclusde:

- The properties of the nanocomposite approach the ones of the constant size nanoparticles with decreasing the dispersion of particle sizes;
- Increase of the size distribution width increases the coercivity (i.e. width) of the ferroelectric hysteresis, but the hysteresis width decreases for the maximum particle radius, which is significantly smaller than dispersion of the distribution function.

[1] A. Morozovska *et al.*, "Analytical description of the size effect on pyroelectric and electrocaloric properties of ferroelectric nanoparticles," *Phys. Rev. Mater.*, vol. 3, no. 10, p. 104414, 2019
[2] H. Shevliakova *et al.*, "The influence of the distribution function of ferroelectric nanoparticles sizes on their electrocaloric and pyroelectric properties," 2020, arXiv:2004.10871v1 [cond-mat].

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