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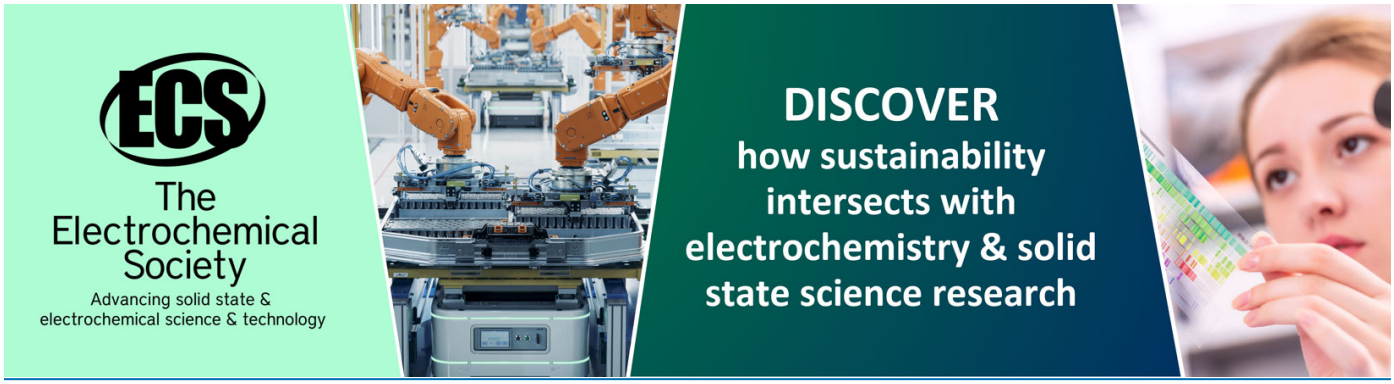

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Investigation of the electrocaloric effect in strontium barium niobate (SBN) ceramics with rare-earth dopants

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Abstract. In ceramics, based on a solid solution of strontium barium niobate (0.7SBN) doped with cerium and gadolinium in various concentrations, an investigation was made of dielectric constant, electrical polarization, and the electrocaloric effect. For 0.7SBN ceramics, it was found that the addition of cerium (0.2%) leads to a decrease in the electrocaloric effect compared to pure 0.7SBN, and the addition of gadolinium (<1%) to an increase in the electrocaloric effect.

In the recent decades, due to the decreasing size and increasing power of electronic components the problem of cooling and temperature control is one of the hottest in the modern electronics and electrical engineering. The effective heat transformation could be implemented in the solid state structures using electrocaloric effect [1, 2]. Many laboratories in the world are engaged in developing new cooling principles based on the use of the electrocaloric effect. One of the most important tasks is still the search and development of new highly effective electrocaloric materials. Now researchers are very interested in lead-free materials based on solid solutions of barium strontium niobate and titanate with various dopants. According to previously published information, the addition of cerium (Ce) in monocrystals of strontium barium niobate leads to an increase in the electrocaloric effect [3], and the addition of gadolinium (Gd) to an increase in the pyroelectric effect [4]. Since the pyroelectric effect is proportional to the electrocaloric effect, it is logical to assume that materials possessing a large pyroelectric effect will have a greater electrocaloric effect. But in previous works, comparative data on the magnitude of the electrocaloric effect in pure and doped strontium barium niobate ceramics and single crystals were not given. In this paper, we investigate and compare the dielectric and electrocaloric properties of ceramics based on strontium barium niobate (SBN), pure and doped with various rare-earth metals (Ce, Gd) at different concentrations.

For research, we chose a solid solution SBN with 70 percent of strontium. The temperature of the phase transition of this composition is close to room temperature, which is convenient for measurements and further use in solid-state cooling elements.Sr0.7Ba0.3Nb2O6 ceramics were fabricated by the solid-state reaction method. The raw materials of BaCO3 and Nb2O5, SrCO3 and Nb205 were grinded by planetary micro mill Fritsch "PULVERISETTE 7 premium line" for 20 min in distillated water using zirconia balls of 3mm diameter as milling medium. The resultant mixtures were calcined at 1200 °C for 2 hours in air and the resultant BaNb2O6 and SrNb2O6 were milled again.

Then, the resulting materials were mixed in the required stoichiometric proportions and the necessary amount of rare earth oxides (CeO2 and Gd2O3) was added therein. After grinding granulation using 4 wt% aqueous solution of methylcellulose binder-lubricant, the powders were dry-pressed into a disc with a diameter of 10 mm and a thickness of 1 mm under a pressure of 6 MPa. The green samples were sintered at 1350 °C in air atmosphere and then cooled in furnace. The sintered samples were double-side polished to thicknesses 0.5 mm gradually. The obtained ceramic samples are shown in table 1.

Table 1. Designation of studied materials.

Designation	Composition
0.7SBN	$Sr_{0.7}Ba_{0.3}Nb_2O_6$
0.7SBN – 0.2%Ce	~ $Sr_{0.698}Ce_{0.002}Ba_{0.3}Nb_2O_6$
0.7SBN – 0.2%Gd	~ $Sr_{0.698}Gd_{0.002}Ba_{0.3}Nb_2O_6$
0.7SBN – 1%Gd	~ $Sr_{0.69}Gd_{0.01}Ba_{0.3}Nb_2O_6$
0.7SBN – 5%Gd	~ $Sr_{0.65}Gd_{0.05}Ba_{0.3}Nb_2O_6$

First, we investigated the temperature dependence of the dielectric constant in our materials. To study the dielectric constant, we used Agilent E4980A Precision LCR Meter. Conductivity measurements of the samples showed a resistance value greater than 0.5 teraohm. Since the SBN samples are aging, in order to avoid the effects of aging when measuring the dielectric constant in the small-signal mode, the measurements were carried out in a mode of temperature decrease after heating the sample above the Curie point [5]. In measurements of electrical polarization in the mode with the using full voltage amplitude, the aging effects of the samples do not affect the values of the electric polarization. Figure 1 presents the temperature dependence of dielectric constant for strontium barium niobate ceramics with rare-earth dopants.

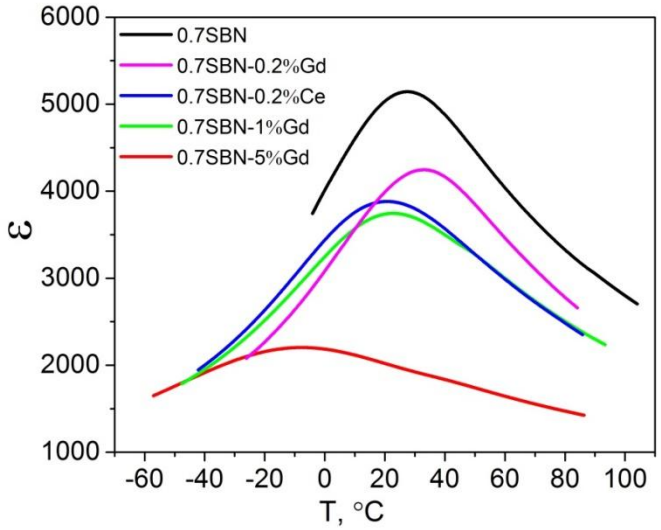

Figure 1. The temperature dependence of dielectric constant for strontium barium niobate ceramics with rare-earth dopants.

It can be seen from the curves that additions of rare earth dopants lead to a decrease in the permittivity as compared to the pure composition 0.7SBN ceramics.

The ferroelectric hysteresis loops were measured at 10 Hz within -50 ~ 80 °C using a Sawyer–Tower circuit based on the thermostatic bath Julabo FP40-MA Refrigerated/Heating Circulator,

arbitrary waveform generator Agilent 33522A, a high-voltage amplifier Trek 609E-6, nanovoltmeter Agilent 34420A for temperature control and Agilent MSOX2004A Mixed Signal Oscilloscope for observing ferroelectric hysteresis loops. The temperature step at which each hysteresis loop was taken was 0.5 degrees. Figure 2 presents ferroelectric hysteresis loops at some different temperatures for strontium barium niobate ceramics with rare-earth dopants.

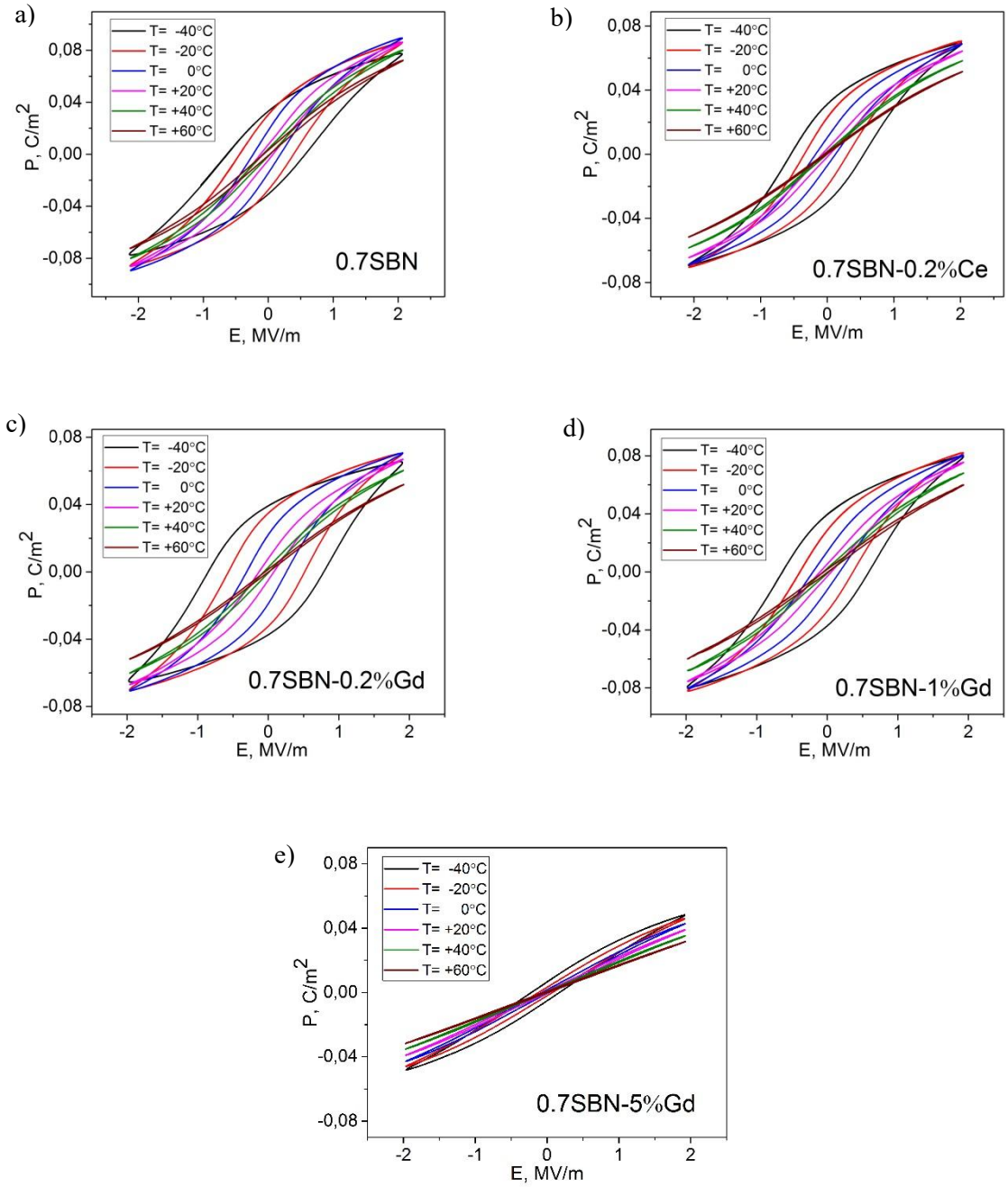

Figure 2. Ferroelectric hysteresis loops at some different temperatures for ceramic samples based on 0.7SBN (a), 0.7SBN-0.2%Ce (b), 0.7SBN-0.2%Gd (c), 0.7SBN-1%Gd (d) and 0.7SBN-5%Gd (e).

From these dependences, well noticeable decrease in the area of the ferroelectric hysteresis loop at the transition from the ferroelectric phase to the paraelectric phase. It should be noted that there is a large difference in the hysteresis loops in the ferroelectric phase and in the paraphrase for 0.7SBN – 0.2%Gd ceramic. Figure 3 presents the dependence of electric polarization versus temperature at different electric field for strontium barium niobate ceramics with rare-earth dopants.

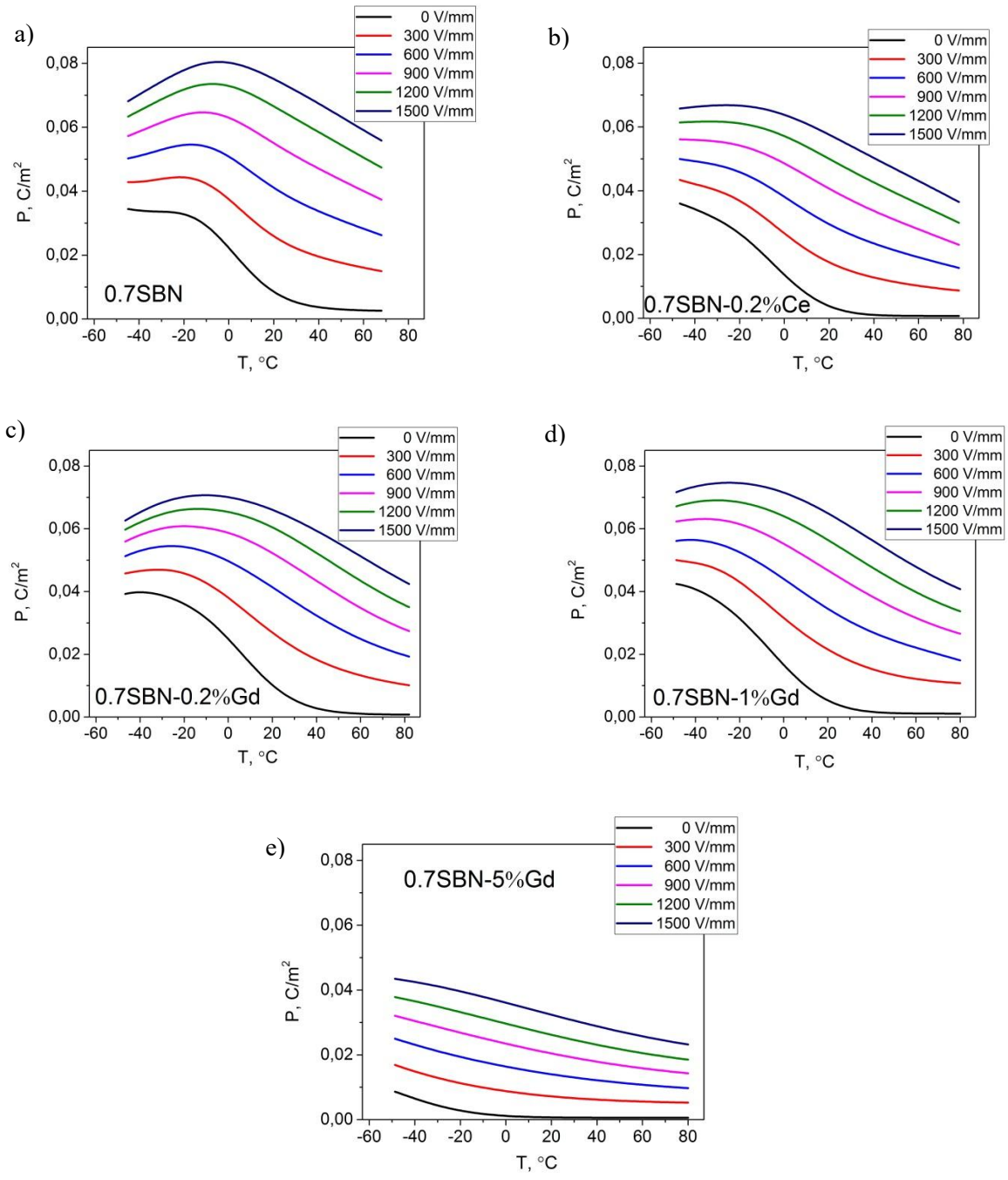

Figure 3. The dependence of electric polarization versus temperature at different electric field for ceramic samples based on 0.7SBN (a), 0.7SBN-0.2%Ce (b), 0.7SBN-0.2%Gd (c), 0.7SBN-1%Gd (d) and 0.7SBN-5%Gd (e).

Based on the thermodynamic Maxwell relation and the obtained temperature dependences of the electric polarization, the electrocaloric adiabatic ΔT was calculated using the following formula:

$$\Delta T = -\int_0^{E_1} \frac{T}{\rho C_E}\left(\frac{\partial P(T,E)}{\partial T}\right)_E dE \quad (1)$$

where ρ is the measured density and CE is the specific heat under constant electrical fields. The calculation used the density value of 5328 kg/m3 and the value of specific heat 440 J/kg*K. The maximum value of the electric field E1 was 1500 V/mm. Figure 4 presents the temperature dependence of the electrocaloric effect for strontium barium niobate ceramics with rare-earth dopants.

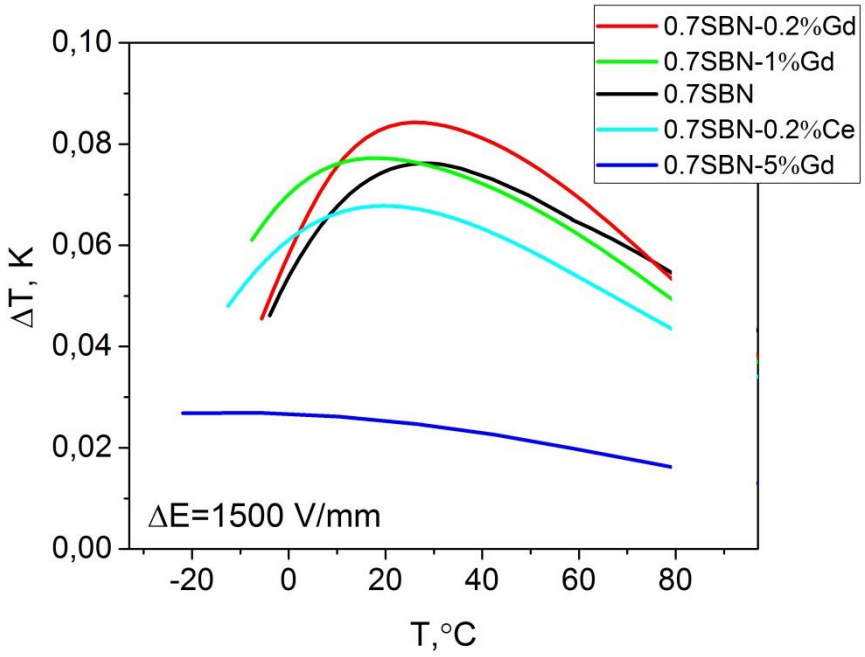

Figure 4. The temperature dependence of the electrocaloric effect.

From the analysis of the obtained dependences, it can be concluded that the addition of cerium in our ceramics leads to a decrease in the maximum magnitude of the electrocaloric effect as compared to pure 0.7SBN. The addition of gadolinium (<1%) leads to an increase in the maximum the magnitude of electrocaloric effect, which agrees well with the assumptions advanced in article [4]. The maximum magnitude of the electrocaloric effect among all our ceramics was obtained in the composition with 0.2% gadolinium supplement.

Acknowledgments
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