

Tuning relaxor and magnetic properties of complex perovskites by varying the compositional ordering degree

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Ferroelectric ternary perovskite oxides of the $PbB'_{1-m}B''_mO_6$ ($m=1/3$ or $1/2$) type, are widely used as components of various functional materials exhibiting giant dielectric, electrostrictive, pyroelectric, and piezoelectric responses. Dielectric properties of these oxides, especially of the 1:1 type perovskites ($m=1/2$) depend crucially on the long-range ordering degree S of B' and B'' cations. While in the highly-ordered state a sharp ferroelectric or antiferroelectric phase transition takes place, in the disordered state a relaxor state is observed, characterized by a diffuse and frequency-dependent maximum of the dielectric permittivity.

Previously, to change the S values of $PbB^{3+}_{1/2}B^{5+}_{1/2}O_3$ perovskites a long-time annealing was used. Later sintering in the presence of liquid-phase as well as variation of the conditions of either the crystal growth or high pressure synthesis were successfully used to change the ordering degree of B -site ions in $PbB^{3+}_{1/2}B^{5+}_{1/2}O_3$ perovskites with $B^{3+}=Fe, Sc, Yb$; $B^{5+}=Nb, Ta, Sb$ [1, 2]. Recently it was found out that high-energy mechanical activation during mechanochemical synthesis stimulates disordering of B^{3+} and B^{5+} ions in ceramics of some 1:1 type perovskites. In some cases it is possible to vary substantially the S values and correspondingly both the temperature and diffusion of dielectric permittivity maxima in these ceramics by changing the regimes of the mechanochemical synthesis and/or using different starting materials (either oxides or preliminary synthesized $B^{3+}B^{5+}O_4$ precursors) [3]. The parameters of the dielectric spectra of the samples exhibiting a relaxor-like behavior also depend on the conditions of the mechanochemical synthesis. Interestingly, the use of mechanochemical synthesis enables one to modify substantially relaxor properties of ceramics of the disordered perovskites $PbFe^{3+}_{1/2}Ta^{5+}_{1/2}O_3$ and $PbMg_{1/3}Nb_{2/3}O_3$. This effect is believed to be caused by the changes in the degree of the short-range ordering [3].

Ordering of Fe^{3+} and B^{5+} ions in $PbFe^{3+}_{1/2}B^{5+}_{1/2}O_3$ ($B^{5+}=Nb, Ta, Sb$) perovskite multiferroics is believed to have an impact on their magnetic properties, as such ordering changes the number of magnetic neighbors around each Fe^{3+} ion. The effect of compositional long-range ordering on the magnetic phase transition temperature T_N was observed in solid solutions of highly-ordered perovskite $PbFe^{3+}_{1/2}Sb^{5+}_{1/2}O_3$ [2]. On the other hand substantial changes in T_N values of disordered $PbFe^{3+}_{1/2}B^{5+}_{1/2}O_3$ perovskites-multiferroics ($B^{5+}=Nb, Ta$) obtained by mechanochemical synthesis seem to be caused by the changes in the degree of the short-range ordering [4].

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1. I.P. Raevski, V.Y. Shonov, M.A. Malitskaya et al, *Ferroelectrics* **235**, 205(1999).
2. I.P. Raevski, A.V. Pushkarev, S.I. Raevskaya, et al, *Ferroelectrics* **501**, 154 (2016).
3. S.I. Raevskaya, A.A. Gusev, V.P. Isupov, et al, *Ferroelectrics* **525**, 37 (2018).
4. A.A. Gusev, S.I. Raevskaya, V.V. Titov, et al, *Ferroelectrics* **496**, 231 (2016).