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Kinetics of Degradation Phenomena in Modified Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O₄ Ceramics

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Semiconductor spinel ceramics are one of the most perspective materials for device application as negative temperature coefficient thermistors. To eliminate the degradation, the method of chemical modification of ceramics is used. Synthesis of modified thermally-sensitive elements based on Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O₄ ceramics was performed owing to technological conditions, the content of NiO phase (1 % - batch 1, 8 % - batch 2, 10 % - batch 3, 12 % - batch 4 and 12 % - batch 5 obtained at different amounts of thermal energy transferred at sintering) having decisive role on final ceramics structure.

The results of ageing tests were controlled by relative resistance drift (RRD) caused by ceramics storage at the temperature of 170 °C. With a purpose of adequate mathematical modelling of the kinetics in studied ceramics, the numerical values of different fitting parameters in the typical relaxation functions (RF) were calculated to minimize the mean square deviation of experimentally measured points from chosen RF. It is well known this kinetics behaviour in spinel-type ceramics can be adequately described by stretchedexponential relaxation function $y=\eta(t)=a(1-exp[(-t/\tau)^{\kappa}])$ at $0<\kappa<1$. Extraction of additional NiO phase from Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O₄ ceramics enlarges the dispersivity of the system, while the monolithization of ceramics causes an opposite effect. The ceramics samples of batch 3 demonstrate the best suitability for stretched-exponential RF. Non-exponentionality index κ grows from 0.10 (batch 1) to 0.66 for batch 2, the similar increase being character for time constant τ too. However, the further increase in NiO content from 10 (batch 3) to 12 % (batches 4 and 5) is associated with principally different processes of microstructural evolution corresponding to monolithization. The nonexponentionality index κ is most close to 1 (κ = 0.66). Despite nearly the same value of non-exponentionality index $\kappa = 0.46$, the time-constant τ decrease from 189.2 for batch 4 to 65.5.2 h for batch 5 samples. The parameter a, which reflects structural perfectness of ceramics, gives a good correspondence between RRD values for all batches and decrease from 43.5 (batch 1) and 6.45 (batch 2) for fine-grain ceramics with small amount of NiO phase to 3.52 (batch 3) and 3.13 (batch 4) for monolithized ceramics. For batch 5 ceramics this value increases to 20.77 at smaller τ = 65.5 h in respect to increase in RRD up to 18%.