Nanovoid Characterization of $NiMn_2O_4$-$CuMn_2O_4$-$MnCo_2O_4$ Ceramics

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Functional temperature-sensitive ceramics based on mixed transition-metal manganites is one of the typical representatives of topologically disordered substances. In bulk ceramics a significant shrinkage of the atomic structure occurs, eventually leading to more or less complex pore topology. These pores (voids) along with specific vacancy-type defects represent free-volume structure of ceramics. The main aim of this work is free-volume or nanovoid characterization of functional oxide materials taking the example of $Cu_{0.4}Co_{0.4}Ni_{0.4}Mn_{1.8}O_4$ ceramics in macro- and micro modifications.

It is shown, that the $Cu_{0.4}Co_{0.4}Ni_{0.4}Mn_{1.8}O_4$ ceramics contained large grains (~10 μm) as well as relatively sharp grain boundaries. So-called "closed" pores have a spherical form and are located mainly near grain boundaries. The $Cu_{0.4}Co_{0.4}Ni_{0.4}Mn_{1.8}O_4$-macro and $Cu_{0.4}Co_{0.4}Ni_{0.4}Mn_{1.8}O_4$-micro ceramics differ only by pores. The neatly shaping grains with comparatively tiny pores (~1 μm) are characteristic for $Cu_{0.4}Co_{0.4}Ni_{0.4}Mn_{1.8}O_4$-micro samples, while $Cu_{0.4}Co_{0.4}Ni_{0.4}Mn_{1.8}O_4$-macro ceramics contain similar crystalline grains with larger pores (reaching in size up to ~10 μm). Open pore size distributions cover significant amount of charge-transferring nanopores depending on sintering conditions and very small number of communication mesopores. The $NiMn_2O_4$-$CuMn_2O_4$-$MnCo_2O_4$ ceramics practically do not possess outside-delivering macropores depending on specific surface area of milled powder. Thus, $Cu_{0.4}Co_{0.4}Ni_{0.4}Mn_{1.8}O_4$ ceramics exhibit so-called one-modal pore size distribution with maximum position near 2 nm and double-maximum near 2.3 and 5.5 nm for $Cu_{0.4}Co_{0.4}Ni_{0.4}Mn_{1.8}O_4$-macro and -micro ceramics, respectively.

Free volume and nanovoids size in studied ceramics are studied also with positron annihilation lifetime measurements. Obtained results are interpreted in terms of unified multi-channel positron annihilation model involving both positron trapping and ortho-positronium decay modes. The shortest component in the lifetime spectra reflects mainly microstructure specificity of the spinel structure with character octahedral and tetrahedral cation vacancies. The extended defects near grain boundaries are supposed to be responsible for middle component at the level of 0.4 ns. The small third component is due to "pick-off" annihilation of o-Ps in the intergranual nanovoids. The observed o-Ps lifetime ~1.8 ns is related to the nanopores with radius of ~2.7 nm based on classic Tao-Eldrup equation.