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Features of structural changes in mechanically activated powders of $Nd_{1-x}Ca_xMnO_{3+\delta}$ solid solutions

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Abstract

The influence of mechanical activation on the crystal structure, oxidation properties, the chemical activity of $Nd_{1-x}Ca_xMnO_{3+\delta}$ (x = 0.0; 0.1) solid solutions in the temperature range T = 20-1180 °C was studied. The orbital order–disorder transition (peculiar to rare earth manganites) was found to shift along the temperature axis with increasing grinding duration. The shift of the transition temperature was caused by change in the chemical composition of mechanically activated samples due to either oxidation of the material or change in the cation ratio of the main phase. Change in the chemical composition of the samples was resulted from intensification (under mechanical activation) of chemical reactions between the ions constituting the manganite (Ca^{2+}, Nd^{3+}, O^{2-}) and the air components (water, carbon oxides, oxygen) on the surface of particles. Mechanical activation had a different effect on the sinterability of the samples $NdMnO_{3+\delta}$ and $Nd_{0.9}Ca_{0.1}MnO_{3+\delta}$. Upon heating mechanically activated $NdMnO_{3+\delta}$, the drowth of the coherent scattering regions (CSR) did not occur in the range 20<T<700 °C but it proceeded rapidly when the temperature was increased above 700 °C regardless of the grinding size. As for the sample $Nd_{0.9}Ca_{0.1}MnO_{3+\delta}$, the intensity of CSR growth decreased with increasing duration of grinding. The formation of calcium-containing metastable phases in the surface layer of grains was the factor that retarded the growth of CSR. With the increase in the layer thickness the temperature region of existence of nanostructured state expands.