26th Congress of SCTM

Sept. 20-23, 2023, Metropol Lake Resort, Ohrid, N. Macedonia

Calcium Containing $ReAlO_3$ (Re = La, Gd) Perovskites. Mechynosynthesis, Morphology and Electrochemical properties

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Rare-earth aluminates ($LaAlO_3$ and $GdAlO_3$) and their calcium-substituted derivates ($La_{1-x}Ca_xAlO_{3-\delta}$; x = 0.05, 0.10, 0.15 and 0.20; $Gd_{1-x}Ca_xAlO_{3-\delta}$; x = 0.05, 0.10 and 0.15) were prepared via one-step mechanochemical processing of simple oxide precursors at ambient temperature. In the case of mechanochemical formation of the $GdAlO_3$, the reaction is accompanied by Gd_2O_3 phase transformation. The as-prepared and sintered materials were characterized by X-ray diffraction and scanning electron microscopy. Sintering at 1450°C resulted in different porosity of the samples, i.e. dense $LaAlO_3$ (density <95% of theoretical value) relatively porous $GdAlO_3$ ceramics (density <90% of theoretical value) except sintered $Gd_{0.85}Ca_{0.15}AlO_{2.925}$. The electrical conductivity of the sintered samples was investigated by impedance spectroscopy in the temperature range ~350-1000°C in air. Acceptor-type substitution of lanthanum and gadolinium by calcium results in ~3 orders of magnitude increase in both total and bulk conductivity associated with a substantial enhancement in oxygen-ionic transport. Further doping has a limited effect on the electrical transport properties, and electrical conductivity remains nearly composition-independent in the range x = 0.05-0.20 for $La_{1-x}Ca_xAlO_{3-\delta}$ and x = 0.05-0.15 for $Gd_{1-x}Ca_xAlO_{3-\delta}$, respectively. Grain boundaries were demonstrated to have a significant contribution to the total resistivity of prepared calcium-substituted ceramics with grain sizes in the range up to 1.5 μm.

Keywords: Lanthanum/Gadolinium aluminates, Perovskites, Mechanosynthesis, Conductivity, Solid electrolyte

Acknowledgement: This work was supported by the Slovak Scientific Grant Agency VEGA (2/0058/23) and Slovak Research and Development Agency APVV (contracts No. 19-0526 and SK-PT 18-0039).