Tuning the High-Temperature Properties of Perovskite-Related Oxides for Electrochemical Applications

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Complex transition metal oxides with mixed electronic and oxide-ion conductivities attract substantial interest due to their potential application in high-temperature electrochemical devices such as solid-state sensors, oxygen permeation membranes and solid oxide fuel cells (SOFCs). Oxides with the perovskite-related structures are considered as best materials for use in such devices. This is especiallytrue for cathode material in intermediate temperature solid oxide fuel cell (IT-SOFC). Major requirements for cathode material in IT-SOFC include high electronic and oxide-ion conductivity, catalytic activity for oxygen reduction, thermal expansion coefficient (TEC) close to that ofthe electrolyte and inertness toward chemical interaction with the electrolyte [1]. In the present work influence of the crystal structure and chemical composition on the properties of perovskite-related cobalt and copper oxides important for their use as cathode materials for IT-SOFC is discussed.

Complex perovskite-related cobaltates with Co^{3+} fit perfectly to the majority of the requirements for cathode materials for IT-SOFC listed above. However, they possess high TEC due to thermally activated transition between low (LS) and high-spin (HS) state of Co^{3+}. Influence of this transition on high-temperature thermal expansion properties of perovskite-related oxides is discussed using an example of layered $(Pr,Sr)_2(Ni,Co)O_4$ oxides [2]. One of the ways to decrease TEC of cobaltatesis to stabilize HS Co^{3+} in the ground state. Such compounds can be found among cobaltates with the brownmillerite-type structure. We have recently discovered the presence of HS Co^{3+}in the ground state in CoO_6octahedra of $Sr_2Co_{1.2}Ga_{0.8}O_5$with the brownmillerite structure [3]. This cobaltate is found to possess as low TEC as 13.1 ppm K^{-1} (298-1073K).

R_2CuO_4, R – rare-earth cation oxides with layered crystal structures having perovskite slab alternating with rock-salt slab (R=La, so called T-phase) or fluorite slab (R=Nd-Gd, so called T'-phase) are considered as prospective cathode materials for IT-SOFC due to their low TEC (~12 ppm K^{-1}) and moderate high-temperature electrical conductivity (>100 S/cm for Pr_2CuO_4). Correlation between the presence of the particular structural slab in the crystal structure of layered cuprates and their high-temperature oxide-ion conductivity is discussed.

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