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Crystalline Phase Stabilization and Structure Dynamics of Oxide-ion Conducting Bismuth Oxides Doped with Rare–earth Cations

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The interconnection between structural and charge–transport properties of crystalline oxide systems, particularly, towards their potential applications in solid oxide fuel cells (SOFCs) and solid oxide electrolysis cells (SOECs) and related energy conversion devices, is increasingly becoming important in the 21st century as the global requirements for sustainable and technologically efficient renewable energy systems continue to rise [1, 2]. In particular, facile charge transport involving mobile oxide ions (O2–) in potential phase–tuned solid electrolytes is essential for robust energy cycles in SOFCs and SOECs tweaked to operate at intermediate and low temperature regimes (˜600 ℃ down to room temperature) [2–4]. Bismuth–based oxides are of great interest due to the highest O2– conductivity observed in the δ–Bi2O3 phase (with face–centred cubic defect fluorite structure) [5]. Various rare–earth doped CeO2 systems have interesting solid state charge–transport properties attributable to distortions of the fluorite crystal lattice [6]. In this work, single– and double–doped bismuth oxides (with Gd3+ and Ce4+ as substituent cations for Bi3+) were prepared via synthetic manipulations involving citrate–nitrate decomposition reactions in acetic acid medium using metal nitrate precursor salts and citric acid as a complexing agent. Room temperature stable phases were studied upon calcination at 400 ℃ and additional heat treatment (up to 850 ℃). Phase stability and transformation studies were undertaken using powder X–ray diffraction (PXRD) performed ex situ (room temperature) and in situ (variable temperature (VT) up to ˜850 ℃). Phase identifications and crystal structure determinations were pursued within the framework of Rietveld refinement from powder diffraction data [7]. Insights on structure–composition–property relations (as a function of temperature) were gained from case studies of doped oxides employed as solid electrolytes for alternating current conductivity measurements involving electrochemical impedance spectroscopy.

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