Abstract

Oxygen ion conducting electroceramics having the characteristic features of oxygen permeation, oxide ions mobility, structural, thermal and phase stability etc. have drawn considerable attention due to their suitability in device applications. The potential application areas are solid oxide fuel cell (SOFC), gas sensors and oxygen pumps etc. Recently, an important approach for creating intrinsic anion deficiency in the lattice structure leading to oxide ion conduction has come in vogue. Such an approach is expected to ensure fast oxygen ion conduction within lattice structure possibly via hopping. However, acceptable O^{2-} ion transport occurs, as per reports in literature, at relatively higher temperature (≥ 800 °C). On the other hand, structural, thermal and phase stability of the ceramic oxides becomes a crucial issue at higher temperatures. These issues have motivated to opt for fabrication and evaluation of materials having anion deficiency in the lattice itself so as to facilitate O^{2-} ion conduction.

The central idea of the present research work was to examine, analyze and evaluate; (a) the role of inherent lattice oxygen deficiency in oxygen ion transport, (b) effect of oxygen ion deficiency on stability property and (c) ion dynamics and relaxation behavior on electrical transport properties. The overall ceramics such as in perovskite system by creating intrinsic anionic deficiency in the lattice have been realized and optimized so that it may act as showing high ionic conductivity and higher stability possibility. The overall research work comprises of six different chapters via different processing routes; (i) preparation of the system, (ii) comprehensive structural analysis by Rietveld method with the aim to estimate oxygen deficiency and its correlation with microstructure, (iii) thermal and phase stability analysis, (iv) electrical and dielectric study to investigate and understand the ion migration in $ABO_{3-\delta}$ lattice, (v) to observe the thermo-mechanical or thermal-expansion coefficient (TEC) compatibility at elevated temperatures. The later is very important aspect for analyzing the suitability for device application. The electroceramics under study have general formula $AMnO_{3-\delta}$ (A is the alkaline earth metal ~Ba, Sr, Ca and δ is the oxygen deficiency level in the lattice with $0 \leq \delta \leq 0.5$) based system have been prepared by different preparation routes i.e. solid state reaction, high energy ball milling and citrate route in oxidizing medium. The samples obtained via different routes have different crystallite size.

Structural and phase analysis carried out using x-ray diffraction (XRD), vibrational spectroscopy (infrared and Raman) have confirmed single phase perovskite structure with limited oxygen deficiency in the lattice (δ~0.14, 0.08). Microstructure analysis using FESEM, HRTEM/SAED, agree well with XRD results. Thermal analysis (TGA) confirmed intrinsic oxygen non-stoichiometry under thermally activated conditions and also indicated the possibility of reversible oxygen permeation over a heating and cooling cycle whereas DTA results indicated the possibility of reversible oxygen permeation in a heating and cooling cycle. Electrical Analysis using complex impedance, dielectric/modulus spectroscopy and dc/ac conductivity have been carried out for a wide temperature and frequency ranges. The experimental results indicate significant changes in electrical behavior under thermal activation observed in terms of; (i) unusual relaxation behavior attributed to structural distortion and lattice defect as a result of oxygen deficiency, (ii) role of bulk (grain) and brain boundary contribution under different range of temperature (iii) hopping conduction as the primary mode of ion dynamics. Thermo-mechanical compatibility in terms of TEC observed in temperature region 30-1100 ºC suggests the suitability of the electroceramics under study for device applications. Materials under report, in the present studies, appear to have multifunctional property.

Keywords: *Oxygen deficient manganites; structural analysis; oxygen deficiency; relaxation; ion dynamics.*