

PREPARATION AND CHARACTERISATION OF NEW CERAMIC MATERIALS AS FAST ION CONDUCTORS

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Introduction

Solid electrolytes are materials in which either the cations or the anions are mobile and act as charge carriers. They are also known as fast ion conductors. These ionic conductors find applications in batteries, solid oxide fuel cells, sensors and other electrochemical devices. A new family of oxide ion conductors based on bismuth vanadates have generated a lot of interests as their conductivities are two orders of magnitude higher than stabilised zirconia which is currently used in solid oxide fuel cells (Kendall et al. 1996). In our laboratory it has been established that introduction of tetra- and di-valent cations could stabilise the high temperature high oxide ion conducting γ phase to room temperatures (Lee and West, 1993; Lee et al. 1994). However, the doping mechanism was far from being understood. It is thus of interest to further investigate the bismuth vanadate systems using different dopants in the search for better performance materials and greater insight into the formation of these materials.

Materials and Methods

New bismuth vanadate solid electrolytes were synthesised by solid state reactions using high purity oxides or salts as starting materials. Phase purity of these materials and hence the solid solution limits of the various series of materials were determined using X-ray diffraction and scanning electron microscopy-energy dispersive analysis. Differential thermal analysis was carried out on phase-pure materials to study their polymorphism and thermal stability. Electrical properties of the materials were investigated using ac impedance spectroscopy over a frequency range of 10 Hz to 13 MHz while temperature was varied from 150 to 800°C. Electrochemical properties of selected materials were examined using cyclic voltammetry. Various parameters such as pH and electrolytes were studied.

Results and Discussion

Phase diagram studies. Phase diagrams of $\text{Bi}_2\text{O}_3\text{-M}_2\text{O}_3\text{-V}_2\text{O}_5$, $\text{Bi}_2\text{O}_3\text{-MO}_2\text{-V}_2\text{O}_5$ and $\text{Bi}_2\text{O}_3\text{-M}_2\text{O}\text{-V}_2\text{O}_5$ were studied and constructed where possible for trivalent cations B, Cr, Al, Y and rare-earth elements La, Yb, Er, Nd and Gd, tetra-valent cations Si and Sn and monovalent cations Li, Na and K respectively. Solid solution areas varied in sizes and directions depending on the dopants involved, indicating different extent and mechanisms of solid solution formation. For the rare-earth elements, they form very similar solid solution areas and the doping mechanism appears to be primarily

$\text{M}\leftrightarrow\text{V}$. Both β and γ polymorphs have been prepared, depending on material compositions. Of the monovalent cations studied, K failed to form any solid solution in the bismuth vanadate system, probably due to the much larger size of K compared to V. Confusions on the phase identity and stoichiometry of the alkali metal systems were sorted out after detailed EPMA studies. **DTA Studies.** Phase transitions of the different polymorphs were observed and characterised in DTA studies. Transition temperatures generally decreased with increasing dopant concentrations. **Conductivity Studies.** Complex plane plots at $\sim 200^\circ\text{C}$ in ac impedance measurements showed a broadened semicircle with an associated capacitance in the order of $10^{-12}\text{ F cm}^{-1}$ which is a typical bulk value. At higher temperatures, the low frequency spike inclined at about 45° to the horizontal became the dominant feature. Its associated capacitance in the range of 10^{-5} to 10^{-6} F cm^{-1} is characteristic of ionic polarisation phenomena at the blocking electrode and a diffusion-limited Warburg impedance, thus supporting the idea that conduction was purely or predominantly ionic. Arrhenius plots were obtained for all the measurements, and activation energies in the range of 0.5 eV were recorded. For the β polymorphs, one change of slope was seen in the Arrhenius plots while the γ polymorphs generally showed a curvature in the region of the phase transition. Rare-earth doped materials (β phase) appeared to be more reversible in their conductivity vs temperature behaviour although their conductivities ($10^{-4}\text{ ohm}^{-1}\text{cm}^{-1}$) were generally one order of magnitude lower than those of the divalent-doped materials (γ phase). **Electrochemical Studies.** Both abrasive stripping and solid state voltammetry studies have been carried out on the parent as well as doped materials. Quasi-reversible electrode behaviour of Bi_2O_3 was seen using ammonium sulphate as the electrolyte. There was however no detectable reduction/oxidation peaks due to the presence of neither V species nor various dopants in the materials that were studied. An effort in trying to prepare thin films of bismuth vanadates using electrochemical deposition method was not successful.

Conclusions

Bismuth vanadate is a remarkable host that could accommodate dopants of various sizes and charges. Stabilisation of high temperature β or γ polymorph upon successful doping is always accompanied by enhanced conductivity in the new materials. Possible substitution mechanisms are $\text{M}\leftrightarrow\text{V}$, $\text{M}\leftrightarrow\text{Bi}$ and $\text{Bi}\leftrightarrow\text{V}$. Preparation of thin films cannot be accomplished by the method of electrochemical deposition.

References

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