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Variable temperature Raman spectroscopy: a "benchtop" technique to complement synchrotron characterization

Yttria stabilized zirconia (YSZ) is a solid ceramic electrolyte that finds application in commercial high temperature systems such as solid state metal-air batteries or fuel cells operating between 600°C and 1000°C. Its conductivity of 0.01 – 0.1 S.cm⁻¹ in the range 700-1000°C relies on oxygen vacancy diffusion enabled by its δ -phase crystal structure. The δ -phase of Bi₂O₃ shows much potential as an alternative solid oxide electrolyte due to its conductivity of ~ 1 S.cm⁻¹ at 750°C, but this phase is only stable in a narrow temperature range (730°C to 824°C) and it has a large coefficient of thermal expansion (CTE). A common strategy is to use doping of the host oxide to stabilize the desired δ -phase structure at lower temperatures, but this stability is often at the expense of conductivity. The challenge is to find a doping regimen that largely preserves the desired δ -phase and associated higher conductivity levels at more practical temperatures, e.g. in the 300°C to 500°C range.

This paper presents results of conductivity and phase stability investigations for three Bi₂O₃ systems (yttrium-doped Bi₂O₃ [1], the Bi₂O₃-WO₃ system [2] and the Bi₂O₃-Dy₂O₃-Er₂O₃ system [3]) where variable temperature (VT) Raman spectroscopy played a key role in identifying phase transition temperatures and selecting optimal samples for further study at a synchrotron facility. This was specifically useful for cases where evidence for a phase transition or a mixture of phases was not clear in laboratory-scale XRD data due to the small differences in the sample crystal structures and the sensitivity of Raman spectroscopy to local order played a significant role. It is observed that VT-Raman measurements are relatively easy and quick to perform and that simultaneously observed photoluminescence can be highly complementary in cation substitution studies.

References

- [1] M A Kiefer, C Billing, R M Erasmus, W M Mogodi, D G Billing, South African Journal of Chemistry, 76 (2022) 111
- [2] S M Masina, C Billing, R M Erasmus, D G Billing, Journal of Electroceramics, 46 (2021) 47
- [3] S M Masina, C Billing, R M Erasmus, D G Billing, unpublished data

Figures

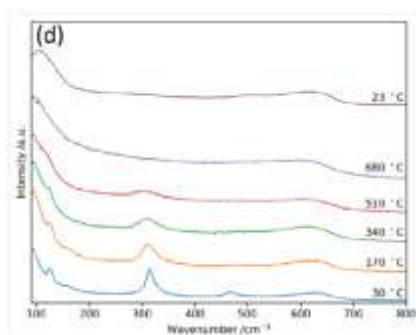


Figure 1: A full variable temperature set of Raman spectra for 17.5 mol% Y³⁺-doped Bi₂O₃ demonstrating tetragonal to cubic phase conversion between 510°C and 680°C. [1]