Local structure in **BIMEVOX** oxide ion conductors

Yajun Yue^{1,3,4}, Ping Miao^{3,4}, Haixue Yan², Isaac Abrahams¹

1. School of Biological and Chemical Sciences, Queen Mary University of London, E1 4NS

2. School of Engineering and Materials Sciences, Queen Mary University of London, E1 4NS

3. Institute of High Energy Physics Chinese Academy of Sciences

4. China Spallation Neutron Source

Introduction

The BIMEVOXes which are based on substitution of V and/or Bi in $Bi_4V_2O_{11-\delta}$ are amongst the best low temperature oxide ion conductors known. Their high conductivity is due to the heavily defective vanadate layer in its Aurivillius structure, as shown in Fig. 1.^[1] However, an understanding of the relationship between local defect structure and conductivity of this important class of materials has never been fully established.

Here we investigate the tetravalent substitution of V⁵⁺ by Ge⁴⁺ with analysis of the local structure using reverse Monte Carlo analysis of total neutron scattering data. Solid state NMR and Raman spectroscopies were also performed to reveal the vanadium atom environment.







Crystallography



Room temperature XRD patterns for $Bi_2V_{1-r}Ge_rO_{5,5-0,5,r}$ (a) compositions (red filled circles mark the a-phase superlattice peaks) and (b) compositional variation of equivalent mean cell lattice parameters.





Crystal structure of g-BIGEVOX35 and derivation of cation coordination geometries from average structural analysis in γ -**BIGEVOX35**



A projection of the vanadate layer (ab plane) in the idealized structure of g-BIGEVOX showing distances between an equatorial vacancy (yellow square) and neighbouring vacancies (sky blue squares)

(010) Cross-section (y = 1) of oxygen density in final folded configurations of BIGEVOX35 at (a) 25 °C and (b) 700 °C.



Radial variation of EV shell content expressed as a ratio with respect to the EV content of the first shell in BIGEVOX35 at 25 °C and 700 °C.



 Table 2
 Nearest M–O shell coordination numbers (CNs) in vanadate
layer of BIGEVOX35

| Cation | CNs | 25 °C | | 700 °C | |
|--------|-----|------------------------------------|---------|------------------|---------|
| | | Fraction (%) | Ave. CN | Fraction (%) | Ave. CN |
| V | 1 | 0.00 ± 0.00 | 4.68(1) | 0.0 ± 0.00 | 4.49(1) |
| | 2 | 0.32 ± 0.17 | | 0.48 ± 0.14 | |
| | 3 | 6.79 ± 0.49 | | 8.46 ± 0.75 | |
| | 4 | 35.11 ± 0.81 | | 43.81 ± 0.61 | |
| | 5 | 40.23 ± 1.07 | | 35.58 ± 0.90 | |
| | 6 | 17.55 ± 0.97 | | 11.67 ± 0.54 | |
| Ge | 1 | 0.00 ± 0.00 | 3.96(1) | 0.0 ± 0.00 | 3.94(1) |
| | 2 | 0.24 ± 0.14 | | 0.22 ± 0.16 | |
| | 3 | 13.01 ± 1.21 | | 14.06 ± 1.60 | |
| | 4 | $\textbf{77.67} \pm \textbf{1.38}$ | | 77.55 ± 1.66 | |
| | 5 | 8.81 ± 1.13 | | 8.00 ± 0.45 | |
| | 6 | 0.27 ± 0.12 | | 0.17 ± 0.05 | |

Conclusions

- A detailed study of the $Bi_2V_{1-x}Ge_xO_{5.5-0.5x}$ solid solution (BIGEVOX) has been made. Compositions in therange $0.0 \le x \le 0.20$ exhibit a pure a-phase structure.
- The high temperature γ -and incommensurately modulated γ' -phases were both modelled using a commensurate tetragonal cell in space group I4/mmm.
- It was found throughout that Ge mainly adopts four-coordinate geometry as predicted, and that oxygen vacancies mainly occur in equatorial sites. Vanadium atoms adopt four-, five- and six-coordinate geometries. No evidence was found for cationic clustering, but some evidence was seen for vacancy ordering, with a non-random deficiency in vacancy pairs in the (100) tetragonal direction.
- The oxide ion conductivity is in the order of 10^{-2} S cm⁻¹ at 600 °C

Refenrences

1. Yue YJ., et al. Journal of Materials Chemistry A. 2022, 10, 3793.