The Characterisation of Anion-vacancy Ordering in the Oxide Ion Conductor $(Bi_2O_3)_{1-x}(Y_2O_3)_x$ by ^{89}Y N.M.R. Spectroscopy

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^{89}Y Magic-angle sample-spinning n.m.r. spectroscopy has been used to show that Y^{3+} ions in cubic, fluorite-like $(Bi_2O_3)_{1-x}(Y_2O_3)_x$ solid solutions are associated with a pair of anion vacancies along <111>.

The local arrangement of anion vacancies and interstitials in metal oxides having fluorite-related structures, *e.g.*, UO_{2+x}, has long been of interest to solid state chemists. Attempts to elucidate the nature of the defect clusters in these materials have centred on neutron scattering and EXAFS techniques, sometimes in conjunction with lattice energy calculations. The general consensus is that the anion vacancies form pairs along either the <111> or <110> directions of the cubic structure, but until now no experimental technique has been able to provide definitive evidence for the existence of one particular form of aggregation. In this communication we describe the unambiguous identification of <111> vacancy ordering about Y in the solid solution $(Bi_2O_3)_{1-x}(Y_2O_3)_x$ by ^{89}Y magic-angle sample-spinning (m.a.s.s.) n.m.r. spectroscopy.

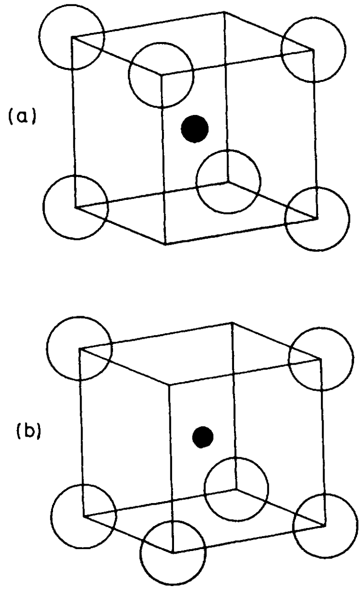

Figure 1. The cation site in the fluorite structure surrounded by six anions and (a) a <111> vacancy pair or (b) a <110> vacancy pair.

Interest in this solid solution stems from its exceptionally high oxide ion conductivity.[1] Neutron scattering studies[2—4] have revealed a cubic fluorite-related structure with an exceptionally high concentration of vacancies on the anion sublattice. Diffuse scattering measurements[3,4] have indicated that vacancy ordering occurs along both the <111> and <110> directions and it has been postulated[3] that the Y^{3+} ion may prefer the centrosymmetric site created by a <111> vacancy pair (Figure 1a), whereas the non-centrosymmetric site between a pair of <110> vacancies (Figure 1b), will be more suitable for Bi^{3+} ions, which are known to take irregular

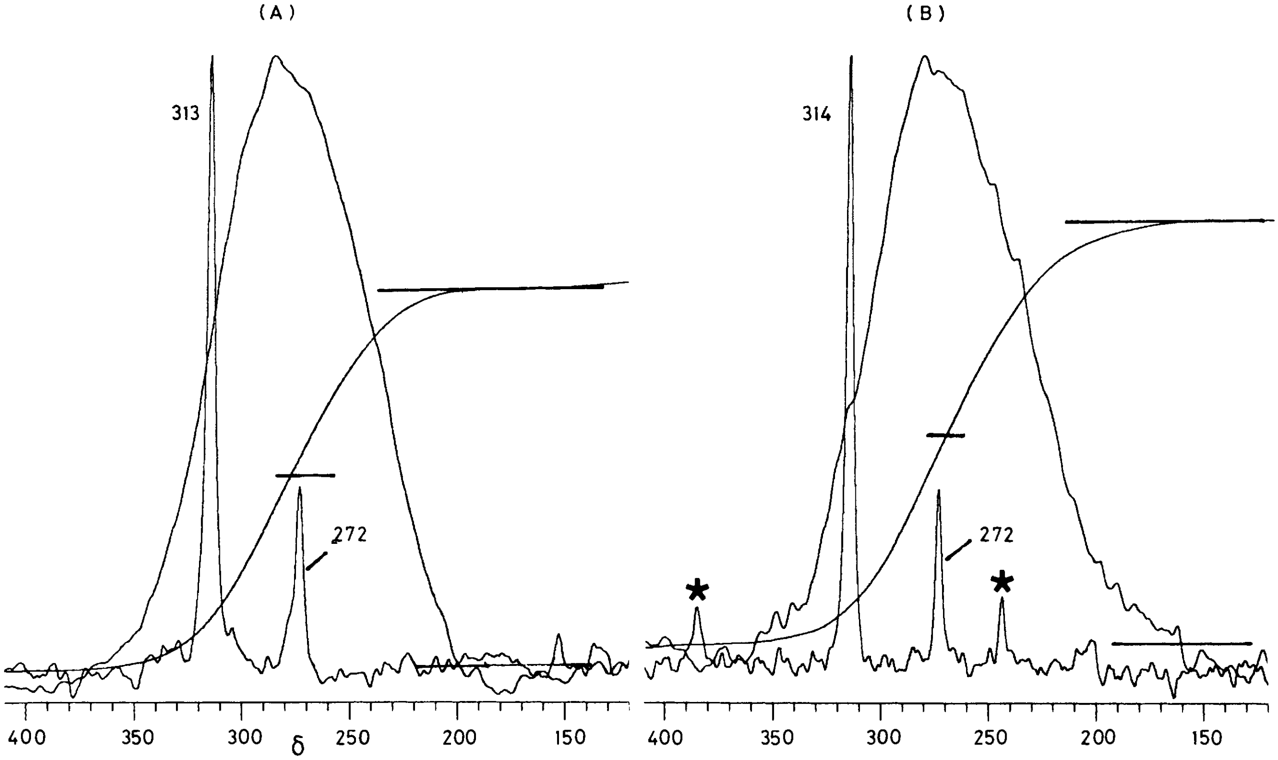

Figure 2. (A) 17.6 MHz and (B) 24.5 MHz ^{89}Y m.a.s.s. n.m.r. spectra of Y_2O_3 (sharp line spectra) and $(Bi_2O_3)_{0.6}(Y_2O_3)_{0.4}$ at 24 ± 2 °C (δ in p.p.m. from 1M YCl_3 in H_2O). The mean centre of gravity of the broad peak (from the half height of the integral) is at 275 ± 2 p.p.m., close to the 272 p.p.m. value found for Y in the <111> site of Y_2O_3 (see text for details). The peaks marked * arise from spinning side bands.

co-ordination geometries. Although a subsequent EXAFS study[5] was consistent with this hypothesis, it remains the result of intuition rather than experiment. However, using the relatively new technique of ^{89}Y m.a.s.s. n.m.r. spectroscopy,[6] we have been able to obtain direct verification of the model.

Spectra were recorded at *ca.* 24 °C by a similar method to that described previously,[6] at 17.6 MHz (8.45 T) and 24.5 MHz (11.7 T). Chemical shifts are relative to an external standard of a 1M solution of YCl_3 in water. Figure 2 shows the spectra of Y_2O_3 at 17.6 and 24.5 MHz, in which two resonances are clearly present, at 314 ± 1 and 272 ± 1 p.p.m. The crystal structure of this compound[7] can be thought of as an ordered, anion-deficient fluorite such that there are two environments for Y^{3+} cations, *i.e.*, they may be surrounded by either a <110> anion vacancy pair or by a <111> vacancy pair, the former type of cation site occurring three times as frequently as the latter. We therefore assign the stronger resonance at *ca.* 314 p.p.m. to the <110> site and the weaker resonance at *ca.* 272 p.p.m. to the <111> site. The spectra of $(Bi_2O_3)_{0.6}(Y_2O_3)_{0.4}$ at 17.6 and 24.5 MHz are also shown in Figure 2. At both field strengths there is a single broad resonance, centred at *ca.* 275 ± 2 p.p.m. Spectra of the 27 and 34% Y-doped materials are very similar in appearance, with the maximum always occurring at *ca.* 275 p.p.m. The large, field-independent (in p.p.m.) linewidth of the Bi-containing sample is expected in a solid solution where a range of local environments (bond angles and bond lengths) will inevitably be present.

We therefore conclude that the Y^{3+} ions in this solid solution are predominantly surrounded by <111> vacancy pairs, as was suggested previously.[3] The Bi^{3+} ions are then likely to be surrounded by the <110> vacancy pairs detected in the neutron scattering experiments, as is required by the conductivity mechanism proposed previously.[3]

We believe these experiments clearly demonstrate the potential of m.a.s.s. n.m.r. in defect chemistry.

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