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A SIMS study of deuterium in $Ba_3(Ca_{1.18}Nb_{1.82})O_{9-\delta}$[†]

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Secondary ion mass spectrometry (SIMS) has been used to study deuterium in single crystals of $Ba_3(Ca_{1.18}Nb_{1.82})O_{9-\delta}$. A deuterium implant was used as a standard for the determination of the deuterium concentration in $Ba_3(Ca_{1.18}Nb_{1.82})O_{9-\delta}$ pre-treated in a D_2O-containing atmosphere. The conductivity of this single crystal has been measured using impedance spectroscopy in a D_2O–nitrogen stream. The values of deuteron concentration, conductivity and diffusivity as well as the constant for the reaction of deuteron incorporation are calculated.

Some oxygen-deficient perovskites have the ability to dissociate water at high temperatures producing protonic defects.[1] These defects are not an essential part of the crystal lattice, although the concentration can be high enough to control the properties of the material, in particular the electrical conductivity. Off-stoichiometric $Ba_3(Ca_{1+x}Nb_{2-x})O_{9-\delta}$ exhibits such behaviour, and at $x=0.18$ this material displays the highest proton conductivity found for ceramic oxides to date.[2] The material is a proton conductor in wet atmospheres from room temperature up to 800 °C[3] although there are contributions from electron holes and oxygen vacancies when the atmosphere is changed.

Secondary ion mass spectrometry (SIMS) depth profiling is an extremely sensitive surface analytical technique capable of determining the elemental and isotopic concentrations of dopant and impurity atoms, within a material, as a function of depth.[4] To obtain a depth profile a specific area is scanned with a mono energetic primary ion beam. As a consequence of the beam–material interaction, the surface of the material is eroded creating a crater; a fraction of the particles sputtered are ions (secondary ions) some of which can be collected and transferred to a mass spectrometer. The chemical and isotopic composition of the material can then be studied as a function of depth. The application of SIMS to the study of high temperature proton conductors has been taken up in recent years; however, as yet there is no unanimous interpretation of the results.[5–9]

Experimental

Three small single crystals of nominal composition $Ba_3(Ca_{1.18}Nb_{1.82})O_{9-\delta}$ were prepared by direct inductive melting in a cold crucible.[10] One of the single crystals, of unknown orientation, was cut in half and polished perpendicular to the cut. One half was implanted with deuterium (1×10^{16} atoms cm^{-2}, 99.9% purity, 50 keV). The other half was pre-treated in vacuum (*ca.* 5×10^{-6} Pa) above 900 °C for 24 h and then annealed for 24 h at 550 °C in a stream of nitrogen bubbled through D_2O (30 °C, $P_{D_2O}=3700$ Pa).This sample was quenched to room temperature. A second crystal was cut, polished and used as a blank. All samples were depth profiled on an Atomika 6500 secondary ion mass spectrometer, using a Cs^+ beam of 15 keV with a current of *ca.* 30 nA. A 2.0 keV electron beam was used for charge compensation. The area scanned was 250 mm x 250 mm and gated down to 25% of the area. A number of negative secondary ion species were followed in the mass spectrometer: $m/z=2$, 16, 17, 18 and 19. The crater depth was measured post-analysis using a surface profilometer.

The electrical conductivity of $Ba_3(Ca_{1.18}Nb_{1.82})O_{9-\delta}$ was measured using impedance spectroscopy. The measurement was carried out on an impedance analyser (Hewlett Packard 4192A). A small single crystal of $Ba_3(Ca_{1.18}Nb_{1.82})O_{9-\delta}$ was cut in the shape of a cuboid. Platinum electrodes were deposited on two opposite faces of the sample and then the specimen was annealed in vacuum (*ca.* 5×10^{-6} Pa) at 900 °C for 24 h. The sample was left at 550 °C for 24 h in a stream of nitrogen bubbled through D_2O ($P_{D_2O}=3700$ Pa) and the conductivity was measured as the samples cooled in the same gas atmosphere. The voltage applied was 50 mV and the frequency range spanned from 10 Hz to 13 MHz.

Results

Mass spectrum

Part of the mass spectrum of $Ba_3(Ca_{1.18}Nb_{1.82})O_{9-\delta}$ treated in D_2O is shown in Fig. 1. The background (*i.e.* no Cs^+ beam on) signal has been included for low *m*/*z* values to show the high level of noise at *m*/*z ca.* 1 (hydrogen). It can be seen that the background contribution for $m/z>1.6$, is small and that a $^2D^-$ signal can be clearly distinguished. Peaks from *m*/*z* 15–20 are very well defined and can be assigned to particular ions (see Table 1), except the signal at *m*/*z* 19 which has been attributed both to $^{19}F^-$[5] and to $^{16}O^1H_3^-$.[8] No signal between 20–22 was detected therefore discarding the possibility of

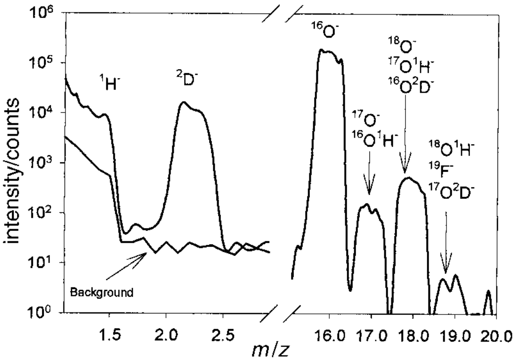

Fig. 1 Mass spectrum of $Ba_3(Ca_{1.18}Nb_{1.82})O_{9-\delta}$ pre-treated in D_2O obtained using a 15 keV Cs^+ beam rastered over an area of 250 µm × 250 µm. The background signal is shown for low *m*/*z* values.

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Table 1 Assignation of negative ions detected in the mass spectrum from a sample annealed in D_2O

m/z	negative ion(s)
2.2	^{2}D
16	^{16}O
17	^{17}O, $^{16}O^{1}H$
18	^{18}O, $^{17}O^{1}H$, $^{16}O^{2}D$
19	$^{18}O^{1}H$, ^{19}F, $^{17}O^{2}D$

exotic ions such as $^{16}O^{2}D_3^-$, $^{16}O^{2}D_2^-$ which have been proposed previously.[8] Some analysis on signals at m/z 16–19 can be made by taking the ratios of the secondary ion intensities (see Table 2). The ratio S_{18}/S_{16} for the blank sample is approximately equal to the natural isotopic ratio (0.2%) of ^{18}O but is clearly higher for the sample annealed in D_2O indicating a contribution from the ion $^{16}O^{2}D^-$. The ratio S_{17}/S_{16} is high above the natural ^{17}O isotopic concentration (0.04%), due to the contribution of $^{16}O^{1}H^-$ indicating that the samples already contained some protons or that the signal 17 is affected by residual gas absorption during analysis.[9] The ratio S_{19}/S_{16}, although low, is still present and is higher for the sample treated in D_2O which could indicate fluorine contamination or $^{17}O^{2}D^-$ contributions.

Deuterium profiles

The depth profiles of three samples, blank, implanted and D_2O annealed are shown in Fig. 2. The $^{16}O^-$ signal was the same for all the samples and is shown as a reference to indicate the Cs^+ beam stability during analysis and also to show that the sputter rate was constant. The implanted sample shows a skewed Gaussian distribution characteristic of a light element implanted into a heavy matrix. The D_2O-annealed sample shows a constant concentration of deuterium, indicating that the sample reached equilibrium with the phase vapour during the anneal. Finally, the blank sample shows a low number of counts for deuterium, as expected since the natural deuterium isotopic concentration is only 0.015%.

Table 2 Secondary ion intensity ratios for the blank and the D_2O annealed sample

	blank (%)	annealed in D_2O(%)
S_{17}/S_{16}	0.095	0.095
S_{18}/S_{16}	0.242	0.346
S_{19}/S_{16}	0.001	0.003

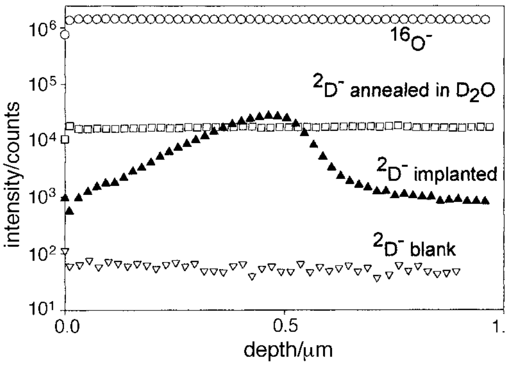

Fig. 2 Depth profile of single crystals of $Ba_3(Ca_{1.18}Nb_{1.82})O_{9-\delta}$. The $^{2}D^-$ signal is shown for three samples: blank, D_2O annealed and D-implanted. The $^{16}O^-$ is shown as a reference.

Deuterium standard

First of all, we estimate the useful ion yield (τ_u) for deuterium implanted in $Ba_3(Ca_{1.18}Nb_{1.82})O_{9-\delta}$ (*i.e.* the fraction of detected $^{2}D^-$ ions per deuterium atom in the sample) according to:

$$\tau_u = \int (^{2}D^-) dy/\phi a f \tag{1}$$

where $\int (^{2}D^-) dy$ = number of $^{2}D^-$ counts during depth profile, y = depth of crater, ϕ is the fluence (1×10^{16} atoms cm^{-2}), a = data acquisition area (the scanned area was gated to avoid crater edge effects), f = fraction of time the mass spectrometer is tuned to count D ions. A value of $\tau_u = 7.79 \times 10^{-6}$ was obtained for our particular SIMS conditions.

Deuteron concentration

Now, knowing the useful ion yield for deuterium in $Ba_3(Ca_{1.18}Nb_{1.82})O_{9-\delta}$, the concentration of deuterons in the D_2O-annealed sample can be quantified according to

$$C_D = \int (^{2}D^-) dy/a y \tau_u f \tag{2}$$

where $\int (^{2}D^-) dy$ is the number of counts during depth profiling, y = depth of crater, a = area of data acquisition, τ_u as estimated with the standard and $f = 0.2$ is the fraction of time D is tuned on the mass spectrometer. For the sample annealed in D_2O at 550 °C the concentration (C_D) is estimated to be 2.71×10^{20} D atoms cm^{-3}.

Conductivity

The impedance plot of $Ba_3(Ca_{1.18}Nb_{1.82})O_{9-\delta}$ measured in wet (D_2O) nitrogen at 320 °C is shown on Fig. 3. All the measurements taken within the range of temperatures studied had the same characteristic shape. Fig. 3 is a typical impedance plot of a single crystal with two main features, a high frequency semicircle and a low frequency curve. The high frequency semicircle is attributed to the single crystal response and can be simply modeled by a resistance and a capacitance in parallel. The capacitance C, can be obtained from this plot since the top of the semicircle corresponds to $Z'' = 1/\omega C$, where ω is the angular frequency. This yields a value of 7.8 pF which is typical of bulk responses. The resistance of the sample corresponds to the intercept of the high frequency semicircle with the real impedance axis. The platinum electrode–single crystal interface is also manifest as a low frequency curve but not enough to study the processes taking place there. The study

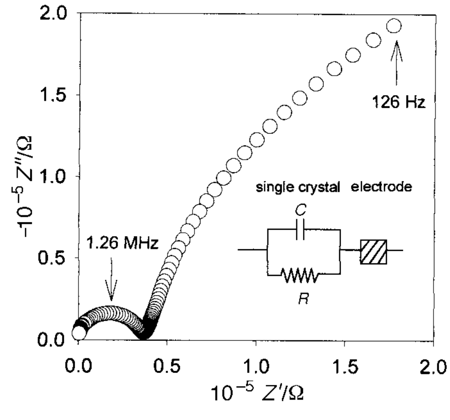

Fig. 3 AC impedance of $Ba_3(Ca_{1.18}Nb_{1.82})O_{9-\delta}$ single crystal in wet (D_2O = 3700 Pa) nitrogen at 320 °C. Some specific frequency values are also indicated. The equivalent circuit is displayed with no *RC* element assigned to the electrode.

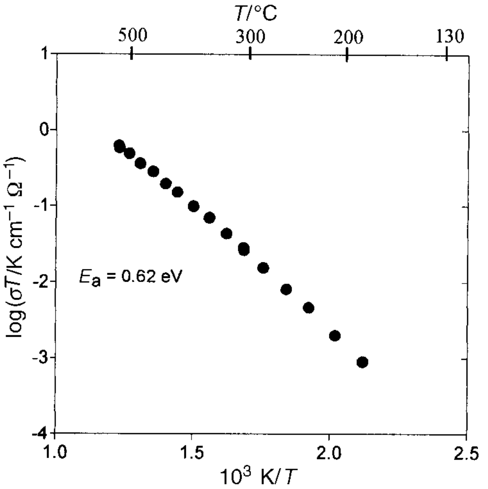

Fig. 4 Arrhenius plot of the conductivity of $Ba_3(Ca_{1.18}Nb_{1.82})O_{9-\delta}$ in D_2O–nitrogen. The activation energy is 0.62 eV.

of these interfaces is better carried out at lower frequencies and will not be further discussed here.

The Arrhenius plot for the conductivity of $Ba_3(Ca_{1.18}Nb_{1.82})O_{9-\delta}$ measured in wet (D_2O) nitrogen ($P_{D_2O} = 3700$ Pa) is shown in Fig. 4. A slight change in slope can be detected above 400 °C suggesting a change in the concentration of deuterons known to be frozen in at lower temperatures.[2] The activation energy between 250 and 550 °C is 0.62 eV comparable to 0.60 eV, the value given for polycrystalline samples at lower temperatures.[2]

Discussion

The deuterium concentration determined for the sample annealed in nitrogen containing D_2O (3.7 kPa) at 550 °C for 24 h was 2.71×10^{20} D atoms cm^{-3}. This is equivalent to 2.06 mol% (relative to Ba), calculated using a value of 5.58 g cm^{-3} for the theoretical density.[11] This is slightly lower than the values obtained by thermogravimetry; according to the results of Krug and Schober,[12] *ca.* 2.5 mol% would be expected. A similar number can be extrapolated from the work of He *et al.* with a single crystal of slightly different composition.[13] Based on gravimetric analysis of wet and dry polycrystalline samples, Du and Nowick[14] calculated a value of 6%, that seems to be constant for different x in $Ba_3(Ca_{1+x}Nb_{2-x})O_{9-\delta}$. The difference with Du and Nowick's work arises as their samples were slowly cooled in wet atmosphere, therefore having the opportunity to create more hydrogen defects. However, it definitely appears that not all oxygen vacancies are filled when water is incorporated [see eqn. (3)]. It has been suggested[15] that these vacancies may form associated complexes of the type $[V_O^{\bullet\bullet}Ca_{Nb}'''V_O^{\bullet\bullet}]^{\bullet}$. Thus, it may be that the number of mobile oxygen vacancies that can migrate to the surface and react is reduced. This agrees well with previous work on $Ba_3(Ca_{1+x}Nb_{2-x})O_{9-\delta}$, where the diffusion coefficient of oxygen vacancies, extrapolated to low temperatures, is low and does not have a considerable contribution to the total conductivity,[13] as was shown for other proton conductors.[16,17]

The elimination of oxygen vacancies by deuteron introduction can be written as (in Kroger–Vink notation),

$$D_2O_{(g)} + V_O^{\bullet\bullet} + O_O^x \rightarrow 2OD_O^{\bullet} \tag{3}$$

$$K = [OD_O^{\bullet}]^2 / [V_O^{\bullet\bullet}] P_{D_2O} \tag{4}$$

where K is the reaction constant and P_{D_2O} is the partial pressure of D_2O at 30 °C = 3700 Pa. Assuming that there is no considerable contribution from electron holes at 550 °C, the electroneutrality condition is,

$$[OD_O^{\bullet}] + 2[V_O^{\bullet\bullet}] = 3[Ca_{Nb}'''] \tag{5}$$

Calculation of the reaction constant, K, at 550 °C yields 1.4×10^{-6} Pa^{-1} which is in excellent agreement with a value of *ca.* 1.5×10^{-6} Pa^{-1} extrapolated from previous work.[12]

From electrical conductivity results, the diffusivity of deuterium, D^*_D can be estimated by means of the Nernst–Einstein equation

$$D^*_D = \sigma Tk / C_D q^2 \tag{6}$$

where σ is the conductivity in D_2O at 550 °C, C_D is the concentration of deuterons, and T, k and q have the usual meanings. A value of 1.7×10^{-6} cm^2 s^{-1} is obtained assuming that the conductivity at 550 °C is predominantly deuteronic. This is comparable to the proton diffusion extrapolated (3×10^{-6} cm^2 s^{-1}) from lower temperatures on $Ca:Ba_3Ca_1Nb_2O_9$.[13]

Conclusions and future work

First of all, we have shown that $Ba_3(Ca_{1.18}Nb_{1.82})O_{9-\delta}$ is able to absorb (heavy) water at high temperatures when exposed to a (heavy) water containing atmosphere. We showed this by comparison of the secondary ion intensity ratios and by direct detection of deuterium using SIMS depth profiling. We have also calculated the total deuteron concentration within a single crystal of $Ba_3(Ca_{1.18}Nb_{1.82})O_{9-\delta}$ using a deuterium implant on the same material as a reference. This concentration can be used in conjunction with conductivity data to estimate the deuteron mobility or diffusion.

Values of the reaction constant K at different temperatures can be obtained so that the enthalpy of the reaction of proton absorption [eqn. (3)] can be estimated. At high temperatures, where equilibrium between D_2O and the samples is rapidly achieved, the estimation of the coefficient of diffusion of deuterium can be measured in a similar manner to that used for the diffusion of oxygen.[16,17] It would also be interesting to measure oxygen diffusion in these materials to estimate to what extent the oxygen (or vacancy) mobility is restricted.

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