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A solution chemistry approach to epitaxial growth and stabilisation of Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> films†Freddy E. Oropeza,<sup>\*a</sup> Ignacio J. Villar-Garcia,<sup>a</sup> Robert G. Palgrave<sup>b</sup> and David J. Payne<sup>a</sup>

Single crystalline pyrochlore Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> films have been grown in three different orientations on yttria-stabilised zirconia at temperatures as low as 600 °C, by using a simple wet chemistry method based on the spin-coating technique. Contrary to free-standing powders and polycrystalline films, epitaxial single crystalline Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> is stable relative to other bismuth titanate compounds at temperatures up to 900 °C. A study of core X-ray photoelectron spectra shows Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> films contain an oxygen deficiency whose concentration depends on the annealing temperature. Based on low-energy ion scattering spectroscopy, it was determined that crystalline surfaces terminate in BiO<sub>x</sub>-like structures.

The pyrochlore bismuth titanate has received significant attention due to its valuable electric properties such as a high dielectric constant and low dielectric loss.<sup>1</sup> In addition, there has been increasing interest in the use of this and other bismuth-based pyrochlore materials as photocatalysts able to drive the oxidation of organics and methanol reforming.<sup>2–4</sup> Pyrochlore compounds have nominal composition A<sub>2</sub>B<sub>2</sub>O<sub>7</sub> and their structure consists of B<sub>2</sub>O<sub>6</sub> octahedral and A<sub>2</sub>O' tetrahedral substructures in an array that can be described as a fluorite cell with a vacancy in the 8a Wyckoff position (A<sub>2</sub>B<sub>2</sub>O<sub>7</sub> vs. 4CaF<sub>2</sub>).<sup>5</sup> The stoichiometry of pyrochlore compounds is often expressed as A<sub>2</sub>B<sub>2</sub>O<sub>6</sub>O', denoting the existence of two distinguishable oxygen sites. It has been theorised that the A<sub>2</sub>O' tetrahedral substructure may lead to electronic stabilisation greater than the loss in Madelung energy, in which case non-stoichiometric pyrochlore compounds can be synthesised.<sup>5,6</sup> In fact, stable phase pure pyrochlore bismuth titanate, Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, can only be

synthesised with a certain amount of bismuth vacancies, which range from 20%–50%.<sup>3,7</sup> Although Hector and Wiggin reported the preparation of this material with a stoichiometric metal composition at 470 °C, increasing the calcination temperature by 10 °C led to the formation of Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>.<sup>8</sup> This is a common impurity found in numerous synthesis procedures.<sup>3,7–9</sup> Here we show that phase pure Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> can be stabilised when grown as an epitaxial layer on yttria-stabilised zirconia (YSZ). Remarkably this is achieved from solution-based chemical deposition, rather than traditional high vacuum physical vapour deposition methods. We suggest that the lowering of energy through epitaxial stabilisation is similar or greater than the energy stabilisation through the creation of bismuth vacancies, thereby allowing the preparation of a bismuth vacancy-free material.

YSZ adopts a fluorite structure with the space group *Fd* $\bar{3}$ *m* with lattice parameter *a* = 0.5125 nm (at 9% Y doping level of the substrates used in the current work). Based on the fluorite cell, pyrochlore Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> adopts a face-centred cubic structure also belonging to the space group *Fd* $\bar{3}$ *m* with lattice parameter *a* = 1.0379 nm.<sup>9</sup> Thus, there is a mismatch of only +1.2% between 2*a* for Y-doped ZrO<sub>2</sub> (1.0250 nm) and *a* for pyrochlore Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>. In addition the cation arrays within the two materials are very similar, which also minimises the chemical mismatch at the interface. Based on these structural resemblances, we demonstrate YSZ single crystals are ideal substrates for the epitaxial growth of pyrochlore films. As confirmed by a detailed X-ray diffraction (XRD) study, single crystalline Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> thin films were successfully grown in three different crystal orientations by using a very simple and low cost wet chemistry method based on the spin coating technique. Annealing in air at temperatures as low as 600 °C were required to crystallise the samples and they were stable up to 900 °C. Core-level photoelectron spectroscopy shows that samples annealed at low temperatures present a high concentration of oxygen vacancies, which strongly decreases after annealing at 900 °C. Study of the surface composition with low-energy ion scattering (LEIS) spectroscopy indicates that the surface of these samples terminates in BiO<sub>x</sub>, which may have important implications for

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† Electronic supplementary information (ESI) available: ESI contains experimental details, X-ray diffractograms of Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> films deposited on (111)-oriented YSZ at 600 °C, 750 °C and 900 °C, and LEIS spectra of all crystalline surfaces studied in this work. See DOI: 10.1039/c4ta04352a

the surface chemistry of this material. The method we report in this communication demonstrates the ease in preparing high-quality, large-area single crystalline epitaxial films, in all three crystallographic orientations. This allows the in-depth characterisation of the electronic properties of the complex oxide  $\text{Bi}_2\text{Ti}_2\text{O}_7$ , an area of research in this system that has been hampered by the lack of high-quality samples produced to date.

A solution of bismuth nitrate and titanium isopropoxide in acetic acid mixed in a 1 : 1 mol ratio was used to spin coat (001), (110) and (111)-oriented YSZ substrates as well as a polycrystalline quartz substrate. After drying at 200 °C, the coated substrates were annealed at temperatures ranging from 600 °C up to 900 °C (see experimental details in the ESI†). Fig. 1(a–c) shows X-ray diffractograms of the films deposited on (111), (110) and (001)-oriented YSZ crystals after annealing in air at 900 °C for 5 hours. The scale of the Y-axis is logarithmic to facilitate the visualisation of relative small features. Aside from the strong Y-ZrO<sub>2</sub> substrate Bragg peaks, the only reflections that can be seen in each diffractogram are those of  $\text{Bi}_2\text{Ti}_2\text{O}_7$  crystals in the same orientation of the substrate, indicating that the atomic planes in the film are parallel to those of the substrate. In the X-ray diffractogram of each orientation,  $\text{Bi}_2\text{Ti}_2\text{O}_7$  film peaks with double Miller indices appear close to those of the substrate since the lattice parameter of the pyrochlore film is almost exactly twice the parameter of the YSZ substrate. Fig. 1(e to g) shows  $\phi$  scans in the [113] direction for  $\text{Bi}_2\text{Ti}_2\text{O}_7$  films deposited on (111)-, (110)- and (001)-oriented YSZ substrates. Reflections from both film and substrate follow the rotational symmetry expected for cubic single crystals, *i.e.* 3-fold for the (111) orientation, 2-fold for the (110) orientation and 4 fold for the (001) orientation. Additionally, reflections from the film occur at the same position as those from the substrate. This clearly indicates that there is in-plane alignment of the crystalline axes of the films in the same direction of those of the

substrate, which confirms that the preparation procedure leads to a single crystalline film epitaxial to the YSZ substrate with the relationship:

$$(111)_{\text{BTO}} \parallel (111)_{\text{YSZ}}, (110)_{\text{BTO}} \parallel (110)_{\text{YSZ}}, (001)_{\text{BTO}} \parallel (001)_{\text{YSZ}}.$$

Fig. 1d shows the characteristic X-ray diffractogram of films deposited on quartz after annealing in air at 900 °C for 5 hours. Besides the expected set of diffraction peaks characteristic of polycrystalline pyrochlore phase, there is a secondary set of peaks belonging to orthorhombic  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ . This secondary phase is commonly observed during the preparation of free-standing pyrochlore  $\text{Bi}_2\text{Ti}_2\text{O}_7$ .<sup>8,9</sup> Structural studies of non-stoichiometric  $\text{Bi}_2\text{Ti}_2\text{O}_7$  have shown that the  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  phase is formed at the expense of the formation of Bi vacancies in the pyrochlore structure.<sup>3,7</sup> In fact, the preparation of a Bi-deficient film by including an excess of the Ti source in the coating solution according to Esquivel-Elizondo *et al.*,<sup>7</sup> leads to the formation of single phase pyrochlore  $\text{Bi}_2\text{Ti}_2\text{O}_7$  film. This suggests the driving force for the segregation of  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  could be the stabilisation of the pyrochlore phase by Bi vacancies. The epitaxial growth on YSZ substrates however allows the preparation of  $\text{Bi}_2\text{Ti}_2\text{O}_7$  with a 1 : 1 metal ratio (rather than having to use a Ti excess) and so there is no secondary phase segregation. The consequences of this are assumed to be an epitaxial film free of metal vacancies. As shown in Fig. S1 of the ESI†  $\text{Bi}_2\text{Ti}_2\text{O}_7$  films crystallise at temperatures as low as 600 °C. It was confirmed that annealing the originally amorphous  $\text{Bi}_2\text{Ti}_2\text{O}_7$  film in the 600 °C to 900 °C temperature range leads to the growth of single crystalline films epitaxial to the YSZ substrate with no secondary phase segregation. The epitaxial growth often brings about a structural stabilization as a result of the low energy of coherent interfaces formed due to the epitaxy.<sup>10</sup>

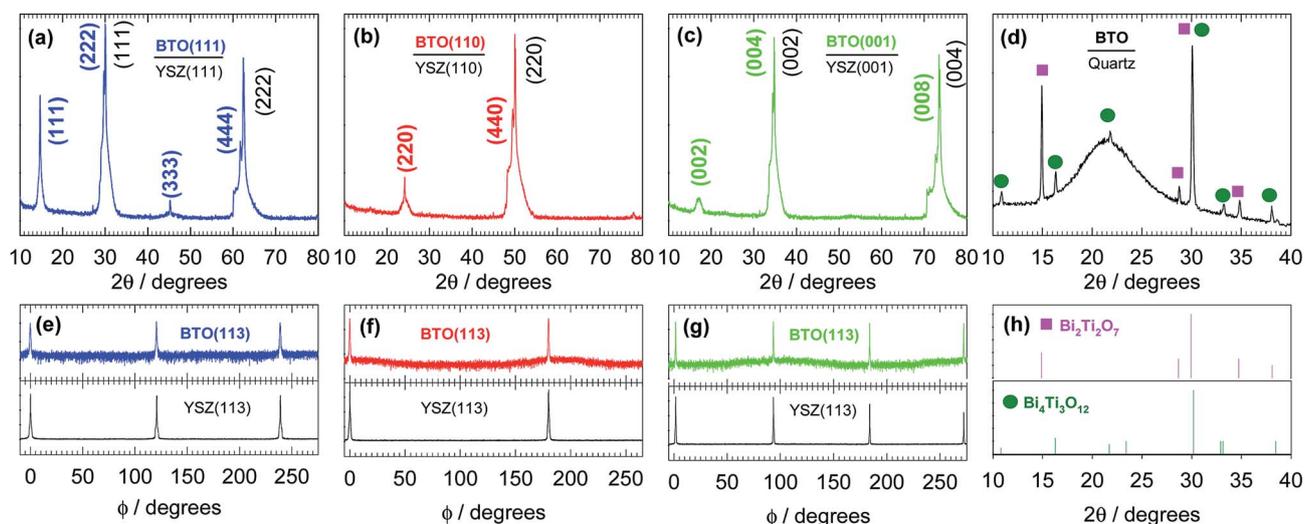


Fig. 1 (a to d) X-ray diffractograms of  $\text{Bi}_2\text{Ti}_2\text{O}_7$  films deposited on (111)-, (110)- and (001)-oriented YSZ and quartz after annealing at 900 °C.  $\phi$  scans in the [113] direction of single-crystalline film and substrate for the (111)-oriented sample (e), (110)-oriented sample (f) and (001)-oriented sample (g). (h) position of the XRD reflections of the two phases detected in the polycrystalline film deposited on quartz.

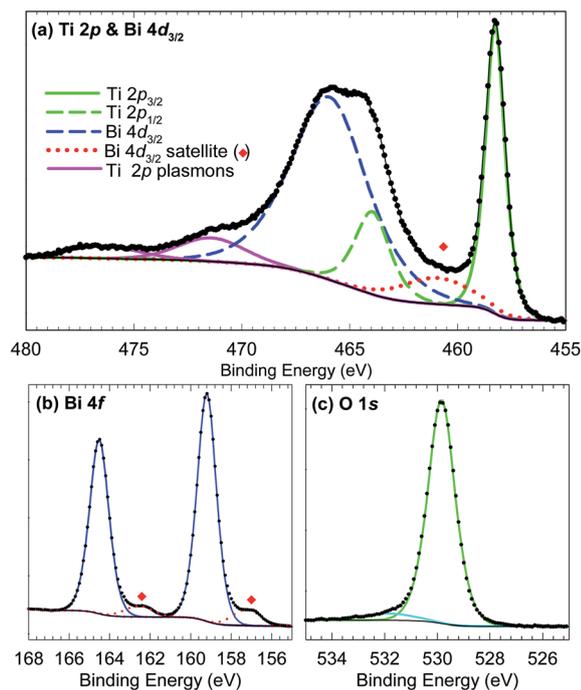


Fig. 2 Peak-fitted principal core lines in XPS of (001)-oriented  $\text{Bi}_2\text{Ti}_2\text{O}_7$  single crystal calcined at  $750\text{ }^\circ\text{C}$ .

Based on our results, we believe that the so-called epitaxial stabilization in the  $\text{Bi}_2\text{Ti}_2\text{O}_7/\text{YSZ}$  system is greater than that brought about by the formation of bismuth vacancies.

The Al  $K\alpha$  X-ray photoelectron spectra (XPS) at normal emission in the O 1s, Ti 2p and Bi 4f regions of (001)-oriented  $\text{Bi}_2\text{Ti}_2\text{O}_7$  calcined at  $750\text{ }^\circ\text{C}$  are shown in Fig. 2 and the core level binding energies, full width half maximums and relative intensities are summarised in Table 1, which also contains data for (110) and (111)-oriented  $\text{Bi}_2\text{Ti}_2\text{O}_7$ . The O 1s peak fits to a component at  $529.84\text{ eV}$  and a second weak component at  $531.84\text{ eV}$ . The shift between the two components of  $2\text{ eV}$  is typically found between intrinsic core lines in oxides and core peaks associated with hydroxide or carbonate surface

contamination. Therefore, the O 1s data in Table 1 only refers to the strong component associated to the metal oxide. The Bi 4f region of the spectrum is dominated by  $4f_{7/2}$  and  $4f_{5/2}$  components at  $159.20\text{ eV}$  and  $164.51\text{ eV}$ . However, there is also a pair of weak but well-defined components shifted by  $2.0\text{ eV}$  to lower binding energy of the main core lines giving rise to distinct low energy shoulders. The Bi  $4f_{7/2}$  binding energy of this component,  $157.20\text{ eV}$ , has an intermediate value between that reported for bismuth metal ( $156.85\text{ eV}$ ) and typical Bi(III) oxides ( $159.0\text{ eV}$  to  $159.8\text{ eV}$ ).<sup>11</sup> The Bi 4f spectra for samples in all three orientations have similar features and the proportion of the low binding energy component is shown in brackets in Table 1. The Ti 2p core lines overlaps with a Bi  $4d_{3/2}$  broad structure. The highest quality peak fit (Fig. 2) includes a strong Bi  $4d_{3/2}$  main component along with a secondary low binding energy component, with area ratio similar to that of the two components in the Bi 4f region. The Ti 2p levels can be fitted with a pair of simple Voigt components for the spin orbit doublet with a Ti  $2p_{3/2}$  binding energy of  $458.22\text{ eV}$ , whose value sits within the range of those found for  $\text{PbTiO}_3$  and  $\text{BaTiO}_3$ .<sup>11</sup> The secondary components found in Bi 4f and Bi 4d core lines indicates the presence of bismuth sites with higher electronic density, which may be associated with the presence of oxygen vacancies, consistent with the low O/Bi atomic ratio compared with that expected for an ideal stoichiometry. There have been several reports on the preparation of oxides having chemical formula  $\text{A}_2\text{B}_2\text{O}_{7-x}$  whose structure may be described as a defect pyrochlore.<sup>12-14</sup> In general, when the cation A is a weakly basic polarisable ion like  $\text{Tl}^+$ ,  $\text{Pb}^{2+}$  or  $\text{Bi}^{3+}$ , oxygen vacancy occurs preferentially in sites having only A cations near-neighbours (*i.e.* oxygen from the  $\text{A}_2\text{O}'$  tetrahedral substructure). The stability of this defect has been attributed to the possibility of A-A bonding across the vacancy.<sup>5,6</sup> Such a stabilization mechanism implies the presence of a considerable electronic density at the oxygen vacancy, which is shared by the bonding A cations, thus creating an A site with higher electronic density. This may be the origin of the low binding energy component we find in the Bi 4f and Bi 4d core level spectra of our samples, suggesting therefore that single crystalline films annealed at low

Table 1 Core level binding energies, FWHM values and relative intensities for single crystalline  $\text{Bi}_2\text{Ti}_2\text{O}_7$

Sample <sup>a</sup>	Bi $4f_{7/2}$		Ti $2p_{3/2}$		O 1s		Bi : Ti : O ratio <sup>c</sup>
	Binding energy <sup>b</sup> (eV)	FWHM (eV)	Binding energy (eV)	FWHM (eV)	Binding energy (eV)	FWHM (eV)	
$\text{Bi}_2\text{Ti}_2\text{O}_7$ (111) $750\text{ }^\circ\text{C}$	159.00 157.65(12.5%)	1.16 2.1	457.84	1.18	529.48	1.27	2 : 1.1 : 5.2
$\text{Bi}_2\text{Ti}_2\text{O}_7$ (110) $750\text{ }^\circ\text{C}$	159.30 157.43(11.0%)	1.20 2.02	458.22	1.53	529.86	1.68	2 : 1.2 : 5.9
$\text{Bi}_2\text{Ti}_2\text{O}_7$ (001) $750\text{ }^\circ\text{C}$	159.20 157.20 (8.1%)	1.12 1.52	458.22	1.04	529.84	1.21	2 : 1.3 : 6.1
$\text{Bi}_2\text{Ti}_2\text{O}_7$ (001) $900\text{ }^\circ\text{C}$	159.39 157.62(2.9%)	1.15 1.22	458.47	1.10	530.04	1.26	2 : 1.1 : 6.6

<sup>a</sup> Crystal orientation is indicated in brackets and the lower value indicates the calcination temperature. <sup>b</sup> Upper value is for the main component, lower value is for the secondary component and the value in brackets refers to the proportion of the secondary component. <sup>c</sup> From XPS using 7.4, 1.2 and 0.66 as sensitivity factors for Bi 4f, Ti  $2p_{3/2}$  and O 1s, respectively.

temperature contain a large concentration of oxygen vacancies. Nonetheless, there seem to be a depletion of oxygen vacancies concentration upon annealing over 900 °C. As shown in Table 1 the fraction of the low binding energy component in the Bi 4f<sub>7/2</sub> spectrum of (001)-oriented Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> film greatly decreases after annealing at 900 °C, which is accompanied by an increase of the O/Bi atomic ratio. Formation of oxygen vacancies in the Ti<sub>2</sub>O<sub>6</sub> octahedral substructure has a higher energetic cost since the stabilization mechanism described above is not possible. Accordingly, the Ti 2p<sub>3/2</sub> does not have any low energy component that could be associated with oxygen vacancies in the Ti<sub>2</sub>O<sub>6</sub> octahedral network of the Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> films.

As shown in Table 1, the Bi : Ti ratio as probed by XPS is larger than the ratio in the precursor solution. Provided the sampling depth for XPS with an Al K $\alpha$  radiation source is approximately 3 to 10 nm, this deviation of the Bi : Ti ratio may be a result of a Bi surface segregation or termination. In order to further investigate this observation we performed a study of the surface composition of the Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> films based on low-energy ion scattering (LEIS) spectroscopy. Fig. 3 (top) shows LEIS spectra of a (001)-oriented Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> surface calcined at 750 °C after oxygen-plasma cleaning and after 10 s and 1000 s Ar<sup>+</sup>-sputtering. On the clean surface, characteristic peaks for bismuth and oxygen can be seen in the He<sup>+</sup> scattering spectrum at 2700 eV and 1200 eV, respectively. Although no spectral peak can be detected in titanium region at 2125 eV, there is a clear background enhancement in this area. This spectrum suggests that the surface of the single crystalline Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> films terminates in a BiO<sub>x</sub>-like structure, but titanium atoms are present in atomic layers directly underneath this termination.<sup>15,16</sup> Very similar results are found in the study of (110) and (111)-oriented Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> samples as can be seen in the Fig. S2.† After less than 10 s sputtering a well-defined titanium peak appears in the LEIS

spectrum of the sample, which is consistent with the presence of Ti directly beneath the outermost atomic layer. As shown in Fig. 3 (bottom), after sputtering for about 600 s the peak area of each region remains steady. We consider that, at this point, preferential sputtering effects are minimised, and therefore the spectrum after 1000 s Ar<sup>+</sup> sputtering is a good representation of the bulk material.

In principle none of the orientations studied can terminate only in BiO<sub>x</sub> (or TiO<sub>x</sub>) as the pyrochlore is not a layered structure. Therefore we hypothesize that there is a surface reconstruction that places Bi<sup>3+</sup> cations at the outermost atomic layer. For pyrochlore Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, bismuth terminated surfaces could certainly lead to lower surface energy and this can be rationalised in terms of the local electronic structure of the Bi<sup>3+</sup> cation. As a free ion Bi<sup>3+</sup> has a configuration 6s<sup>2</sup>6p<sup>0</sup>. It has been shown that for many post-transitional metal oxides, the 6s electrons hybridise strongly with O 2p states to give anti-bonding states of mixed metal 6s–O 2p character at the top of the valence band. These states can further interact with nominally empty metal 6p states to lower the electronic energy and give a directional electron lone pair provided that the cation occupies a site that lacks inversion symmetry.<sup>17</sup> O 2p-assisted Bi 6s–6p hybridisation has been suggested to be energetically favourable in theoretical studies of Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, and related to a strong displacement of Bi atoms from its ideal D<sub>3d</sub> local environment within the pyrochlore structure.<sup>18</sup> However, the lowered coordination at the surface provides non-symmetric sites, thereby allowing 6s–6p hybridisation and a lowering of the internal electronic energy of the cation. This therefore may offer a thermodynamic driving force for a surface reconstruction that places Bi<sup>3+</sup> cations at the surface.

The remarkable difference in composition clearly observed between the bulk and near surface of Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> has never been considered in the numerous theoretical and experimental studies of this material. This characteristic may however have strong implications in the surface chemistry of this material and is therefore an important factor to take into account when considering the interaction of this material with other chemical species. It is indeed very relevant for the current photocatalyst research on Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>.

In summary, single crystalline pyrochlore Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> thin films were grown in three different orientations on Y-stabilised zirconia at temperatures as low as 600 °C, by using a simple wet chemistry method based on the spin-coating technique. YSZ substrate is ideal for the epitaxial growth of pyrochlore Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> due to a high structural coherence and small interface lattice mismatch ( $a_{\text{BTO}} \sim 2a_{\text{YSZ}}$ ). Additionally, the epitaxial growth of Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> on YSZ also brings high epitaxy stabilization, which allows the preparation of metal vacancy-free material. As determined by X-ray photoelectron spectroscopy, films prepared at low temperature present a secondary Bi site with higher electronic density, which we have associated with existence of oxygen vacancies in the Bi<sub>2</sub>O' tetrahedral network. This defect strongly decreases upon annealing at 900 °C in air. Surface composition analysis based on low-energy ion scattering spectroscopy indicates that the surface of the samples prepared by this method terminate exclusively in BiO<sub>x</sub>, which

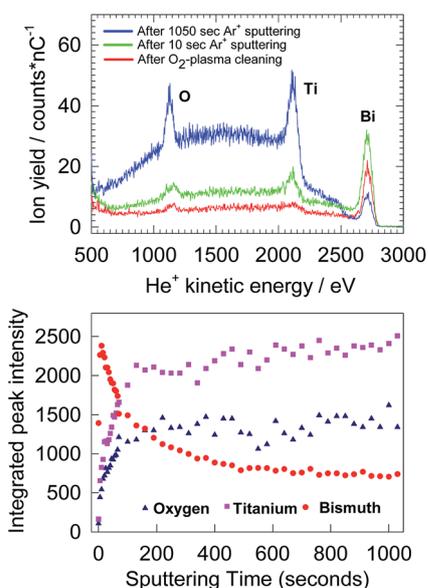


Fig. 3 (Top) LEIS spectrum of (001)-oriented Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> single crystal calcined at 750 °C. (Bottom) integrated peak intensity in LEIS spectrum as function of Ar<sup>+</sup>-sputtering time.

suggests that there might be some sort of surface reconstruction that places bismuth cations in the outmost atomic layer of the  $\text{Bi}_2\text{Ti}_2\text{O}_7$  crystals.

## Conceptual insights

Here we introduce a new simple and low cost wet chemistry method for the preparation of single-crystalline pyrochlore bismuth titanate films, through the epitaxial growth on yttria-stabilised zirconia. We found that the epitaxy stabilises the pyrochlore phase relative to other bismuth titanate phases, which allows an easy preparation of this material with perfect metal stoichiometry and free of secondary phase segregations. A study of the surface composition of  $\text{Bi}_2\text{Ti}_2\text{O}_7$  single-crystalline films based on low energy ion scattering spectroscopy reveals this material has a preferential  $\text{BiO}_x$  surface termination, which may have strong influence on its surface chemistry.

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