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Electronic Supplementary Information for

Tracer diffusion of ^{96}Zr and ^{134}Ba in polycrystalline $BaZrO_3$

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1 Deposition of ZrO_2 films

In order to synthesize a film of $^{96}ZrO_2$ on the BZ pellets the following procedure was developed. Appropriate amount of the ZrO_2 precursor was suspended in excess of concentrated 98% H_2SO_4 in a covered glass and heated to 200 ºC on a magnetic stirrer. After complete dissolution of the precursor (reaction (1)), the resulting slightly yellow transparent solution was slowly evaporated at 200 ºC over excess amount of NaOH solution resulting in hydrated $Zr(SO_4)_2$. The NaOH solution was used to reduce fuming and collect most of the acidic vapour. The white crystalline solid was carefully dried on a hotplate in order to remove traces of H_2SO_4 and then cooled to room temperature. $Zr(SO_4)_2$ was then dissolved in deionized water giving a solution with pH~1-2. The acidic solution was neutralized with 28% NH_4OH until a white fluffy solid precipitated at pH~8 as described by reaction (3). The mixture was carefully dried on a hotplate at 80 ºC resulting in a white $Zr(OH)_4$ amorphous solid. The reaction product $Zr(OH)_4$ was gently mixed with 65% HNO_3 until complete dissolution as shown in reaction (4). Finally, the solvent was evaporated at 110 ºC giving white $ZrO(NO_3)_2 \cdot xH_2O$ crystals. This product was dried at 80 ºC and used further.

$$\mathrm{ZrO_{2(s)} + 2H_2SO_{4(aq)} \rightarrow Zr(SO_4)_{2(aq)} + 2H_2O_{(g)}} \qquad (1)$$

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 $Zr(SO_4)_2 \cdot x\,H_2O_{(aq)}$ (2)

$$Zr(SO_4)_{2(aq)} + 4NH_4OH_{(aq)} \rightarrow Zr(OH)_{4(s)} \downarrow + 2(NH_4)_2SO_{4(aq)} \quad (3)$$

$$Zr(OH)_{4(s)} + 2HNO_{3(aq)} \rightarrow ZrO(NO_3)_{2(aq)} + 3H_2O_{(l)} \quad (4)$$

In addition to the process above, side reactions (5) and (6) occurred producing minor amount of ammonium sulfate and ammonium nitrate, which affected the phase purity of tracer layer produced by the procedure,

$$H_2SO_{4(aq)} + 2NH_4OH_{(aq)} \rightarrow (NH_4)_2SO_{4(aq)} + 2H_2O_{(l)} \quad (5)$$

$$HNO_{3(aq)} + NH_4OH_{(aq)} \rightarrow NH_4NO_{3(aq)} + H_2O_{(l)} \quad (6)$$

The main product $ZrO(NO_3)_2 \cdot xH_2O$ was dissolved in deionized water (0.05 M) and drop casted on $BaZrO_3$ pellets at 90 ºC. The coated pellets were carefully dried at 150 ºC giving a white layer of $ZrO(NO_3)_2 \cdot xH_2O$. Note that the solution had to be used as soon as possible due to the hydrolysis of $ZrO(NO_3)_2 \cdot xH_2O$ in water according to reaction (7)

$$ZrO(NO_3)_{2(aq)} + 2H_2O_{(l)} \rightarrow ZrO_2 \cdot H_2O_{(s)} \downarrow + 2HNO_{3(aq)} \quad (7)$$

The $ZrO(NO_3)_2 \cdot xH_2O$ layer was decomposed at 800 ºC for 3 h in flowing N_2 resulting in a white, dense and homogeneous layer of ZrO_2 (~1-1.5 µm), reaction (8).

$$ZrO(NO_3)_2 \cdot xH_2O_{(s)} \rightarrow ZrO_{2(s)} + \left\langle N_aO_{b(g)} + cO_{2(g)} \right\rangle + xH_2O_{(g)} \quad (8)$$

In addition to the main reaction (8) above, side reactions due to the minor products occurred, reactions (9) – (11)

$$(NH_4)_2SO_{4(aq)} \rightarrow NH_4HSO_{4(s)} + NH_{3(g)} \uparrow \qquad < 300^\circ C \quad (9)$$

$$NH_4HSO_{4(s)} \rightarrow NH_{3(g)} \uparrow + SO_{2(g)} \uparrow + 1/2O_{2(g)} \uparrow + H_2O_{(g)} \uparrow \qquad > 500^\circ C \quad (10)$$

$$NH_4NO_{3(aq)} \rightarrow N_2O_{(g)} \uparrow + 2H_2O_{(g)} \uparrow \qquad < 270^\circ C \quad (11)$$

It is important to note that $BaZrO_3$ is unstable in acidic gases at elevated temperatures.[10] $BaZrO_3$ is highly reactive towards $SO_3(g)$ to form $BaSO_4$ as a side product, reaction (12),

$$BaZrO_{3(s)} + SO_{3(g)} \rightarrow ZrO_{2(s)} + BaSO_{4(s)} \quad (12)$$

The decomposition reaction (8) was performed in a high flow of inert atmosphere in order to avoid formation of barium sulfate.

2 Deposition of BaO films

In order to synthesize BaO films the following procedure was developed. Appropriate amount of $BaCO_3$ was dissolved in aqueous HNO_3, reaction (13). The resulting clear solution was evaporated at 90 ºC. After carefully drying on the hot plate, crystalline solid is obtained as shown in reaction (13). The product is dissolved in deionized H_2O giving a dilute solution (0.015 M) and mixed with citric acid (CA) 0.05 wt% of solution. This solution was used further. Note that CA is used to reduce surface tension for deposition of the solution on the ceramic surface.

$$\mathrm{BaCO_{3(s)} + 2HNO_{3(aq)} \rightarrow Ba(NO_3)_{2(aq)} + CO_{2(g)} + H_2O_{(l)}} \qquad (13)$$

The necessary amount of $Ba(NO_3)_2$ solution was drop casted on the surface of the $BaZrO_3$ pellet at 100 ºC. The coated ceramic was carefully dried on the plate at 110 ºC giving a dense and white layer of $Ba(NO_3)_2$. The coated pellets were further heat treated at 700 ºC for 3 h in flowing N_2 in order to decompose nitrate according to reaction (14)

$$\mathrm{2Ba(NO_3)_{2(s)} \rightarrow 2BaO_{(s)} + 4NO_{2(g)} + O_{2(g)}} \qquad (14)$$

It is important to note that BaO is reactive towards CO_2 in air, and traces of $BaCO_3$ might occur upon cooling and exposure to ambient air.

3 Thin films of the tracers

The homogeneous layers of BaO and ZrO_2 were characterized by EDS and the results are shown in Figure S1. The distribution of the main elements was recorded and filtered separately to give the representative and mono-elemental images. The mapping was performed with ~8 keV electron beam. The thickness of the layers varied 0.8–2 μm. The figure indicate limitation of the SEM equipment used in the thickness region ~1 μm. However, the differences in element concentration from surface to the bulk are obvious. The coated ceramics were used further.

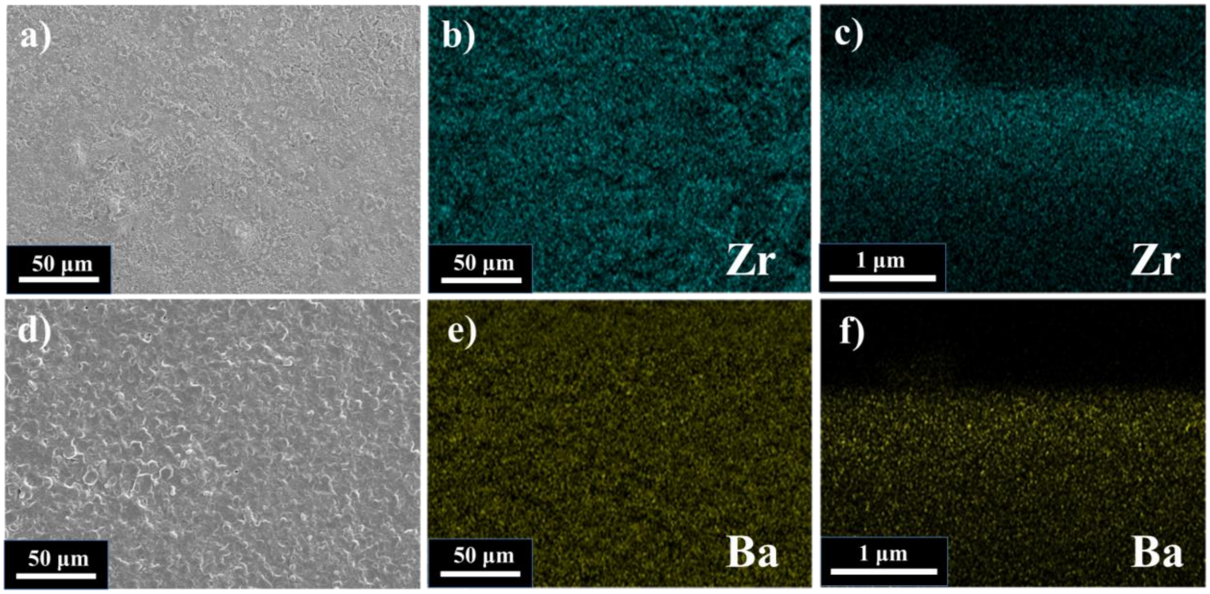

Figure S1. Layers of ZrO_2 (a, b, c) and BaO (d, e, f) on the surface of BZ: a) and d) – SEM images; b) and e) – EDS elemental mapping; c) and f) – EDS cross-section mapping.

4 Fitting procedure of the tracer profiles

The lattice diffusion coefficient constant was evaluated from the slope of the logarithmic concentration versus x^2 (Equation 4). The grain boundary diffusion coefficient was calculated from the shallow part of logarithmic concentration versus and $x^{6/5}$ (Equation 5). The selected depth profile as a scheme for the fitting approach concerning the normalized distribution for ^{134}Ba diffusion in BZ is given in Figure S2. The tracer penetration into the lattice <1 µm is shorter than the average grain size. The lattice diffusion constant was evaluated from the slope of the logarithmic concentration change versus x^2 (see Figure S2b). The grain boundary diffusion coefficient was determined from the shallow part of logarithmic concentration versus and $x^{6/5}$ (see Figure S2c). The diffusion coefficients for all the samples are summarized in Table S1.

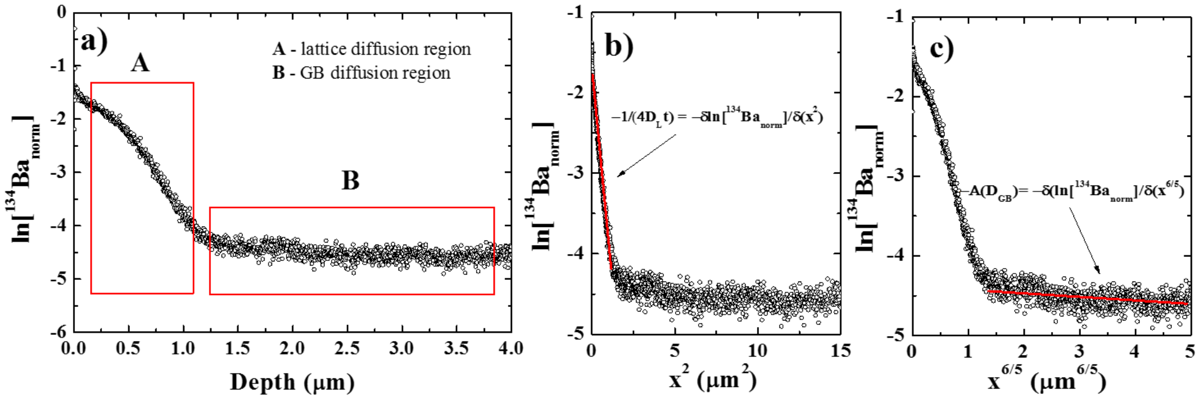

Figure S2. Logarithmic concentration changes of ^{134}Ba in BZ versus depth (a) and modified depth used for the fitting of lattice (b) and grain boundary (c) diffusion coefficients. The sample was annealed at 1050 ºC for 35 h.

The critical parameters α and β were extracted from D_L and D_{GB}, using the following equations

$$\alpha = \frac{s\delta}{2\sqrt{D_L t}} \qquad (15)$$

$$\beta = \frac{s\delta D_{GB}}{2D_L\sqrt{D_L t}} \qquad (16)$$

where, δ=1 nm; *s*=1 and *t* is diffusion anneal time. The critical parameters α and β are summarized in Table S1 for all the samples. α and β represent the ratio of the bulk and grain-boundary diffusion to the effective diffusion coefficient. The estimated values for α is in the range 0.01–0.03 for both tracers and are higher for ^{96}Zr transport. The β values exceed 100 and are higher for ^{134}Ba tracer diffusion. These values demonstrate that the requirements for determination of the grain boundary diffusion is fulfilled.[29]

5 Fitting of the tracer diffusion coefficients to the Arrhenius equation

The fitting of the Arrhenius equation to the experimental data for ^{134}Ba and ^{96}Zr diffusion in BZ are given in Table S1. The data demonstrate that the slope is less for grain boundaries than for the lattice.

Table S1. Experimental conditions for the thermal annealing, and lattice and grain boundary diffusion coefficients and the coefficients α and β data for ^{134}Ba and ^{96}Zr diffusion in $BaZrO_3$.

Sample	**Tracer**	**Time (h)**	**Temperature (ºC)**	**D_L (cm^2/s)**	**D_{GB} (cm^2/s)**	α	β
t1-T1	^{134}Ba	90	1015	$2.78\cdot10^{-15}$	$1.44\cdot10^{-10}$	0.0017	870±70
t2-T2		30	1050	$4.94\cdot10^{-15}$	$1.43\cdot10^{-10}$	0.0020	1000±140
t3-T3		10	1100	$4.76\cdot10^{-14}$	$1.05\cdot10^{-9}$	0.0012	270±20
t4-T4		4	1150	$8.87\cdot10^{-14}$	$2.17\cdot10^{-9}$	0.0014	350±20
t5-T5		2	1200	$2.34\cdot10^{-13}$	$3.25\cdot10^{-9}$	0.0012	1690±2
t1-T1	^{96}Zr	90	1300	$9.64\cdot10^{-16}$	$3.26\cdot10^{-11}$	0.0028	96±4
t2-T2		35	1350	$7.33\cdot10^{-15}$	$1.45\cdot10^{-10}$	0.0023	352±1
t3-T3		10	1400	$1.36\cdot10^{-14}$	$2.37\cdot10^{-10}$	0.0018	394±3
t4-T4		4	1450	$2.14\cdot10^{-14}$	$4.68\cdot10^{-10}$	0.0028	625±1
t5-T5		2	1500	$5.95\cdot10^{-14}$	$8.21\cdot10^{-10}$	0.0024	333±1

Table S2. A summary of the fitting of the Arrhenius equation to the experimental data for both lattice and grain boundary diffusion of both Ba and Zr in polycrystalline BZ.

Tracer	Annealing conditions	Diffusion location	Adj. R^2	Intercept	Error	Slope	Error	D (cm^2 s^{-1})	Error
^{134}Ba	1050 ºC; 35 h	Lattice	0.982	-1.31	0.01	-3.02	0.02	4.94×10^{-15}	1×10^{-15}
		GB	0.868	-4.00	0.05	-0.36	0.02	1.43×10^{-10}	1×10^{-10}
^{96}Zr	1450 ºC; 4 h	Lattice	0.995	-1.04	0.01	-0.81	0.01	2.14×10^{-14}	1×10^{-14}
		GB	0.995	-2.18	0.01	-0.27	0.01	4.68×10^{-10}	1×10^{-10}