

¹³⁴Ba diffusion in polycrystalline BaMO₃ (M = Ti, Zr, Ce)

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Cation diffusion in functional oxide materials is of fundamental interest, particularly in relation to interdiffusion of cations in thin film heterostructures and chemical stability of materials in high temperature electrochemical devices. Here we report on 134 Ba tracer diffusion in polycrystalline BaMO₃ (M = Ti, Zr, Ce) materials. The dense BaMO₃ ceramics were prepared by solid state sintering, and thin films of ¹³⁴BaO were deposited on the polished pellets by drop casting of an aqueous solution containing the Ba-tracer. The samples were subjected to thermal annealing and the resulting isotope distribution profiles were recorded by secondary ion mass spectrometry. The depth profiles exhibited two distinct regions reflecting lattice and grain boundary diffusion. The grain boundary diffusion was found to be 4-5 orders of magnitude faster than the lattice diffusion for all three materials. The temperature dependence of the lattice and grain boundary diffusion coefficients followed an Arrhenius type behaviour, and the activation energy and pre-exponential factor demonstrated a clear correlation with the size of the primitive unit cell of the three perovskites. Diffusion of Ba via Ba-vacancies was proposed as the most likely diffusion mechanism. © 2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). https://doi.org/10.1063/1.5006137

I. INTRODUCTION

 $A^{II}B^{IV}O_3$ oxides are among the most interesting perovskites due to their application in electronics and energy technologies.^{1–4} Among these BaMO₃ (M = Ti, Zr, Ce) comprise a sub group of the $A^{II}B^{IV}O_3$ perovskites which display a wide range of functional properties. BaTiO₃ is one of the classic prototype ferroelectric materials with superior dielectric properties, while acceptor doped BaZrO₃ and BaCeO₃ possess proton conductivity and mixed ionic-electronic conductivity.^{2,4,5} These solid-state proton conductors have attracted considerable attention due to a range of electrochemical applications, such as fuel cells, gas separation membranes and steam electrolysers.^{2,6} Given their importance, the properties of BaMO₃ have been extensively studied experimentally and by first principles calculations.^{2,4,5}

The crystal structure of BaMO₃ perovskites is determined by the size of the M^{4+} (M = Ti, Zr, Ce) cations, and the ambient crystal structure changes from tetragonal, to cubic and orthorhombic reflecting the variation in the Goldschmidt tolerance factor.^{2–4} The high sintering temperature for these oxide materials combined with the volatility of BaO give rise to an interesting defect chemistry as discussed extensively for BaZrO₃ where Ba-deficiency is of importance for the material stability and the mobility of A-cations.⁷ Cation diffusion is of fundamental interest for the understanding of properties and the chemical durability of solids. This is illustrated by the fact that cation diffusion controls sintering and grain growth during materials processing.^{8,9} Further, the importance of cation transport has recently been addressed in relation to 2D electron gas at SrTiO₃/LaAlO₃ interfaces.¹⁰



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Cation diffusion is also vital with respect to the long term stability of these materials as electrolytes in high temperature electrochemical devices. In cases where the ceramics are exposed to large chemical potential gradients, cation transport towards one side may occur if cations are sufficiently mobile inducing kinetic demixing and decomposition.¹¹

To the best of our knowledge, systematic studies of the Ba-diffusivity with respect to the size of the B-site cation in perovskites have so far not been reported. Recently we studied Ba and Zr tracer diffusion in BaZrO₃,¹² and here we report further on ¹³⁴Ba tracer diffusion in two additional materials BaTiO₃ and BaCeO₃. The diffusion data is discussed with respect to the diffusion mechanism supported by previous computational studies^{12,13} and to the size of the primitive unit cell.

II. EXPERIMENTAL

The preparation of the BaZrO₃ ceramics was described elsewhere.⁷ The BaTiO₃ ceramics were prepared by two-step sintering at 1320 °C for 1 min and 1150 °C for 15 h in air. BaCeO₃ was synthesized via solid state reaction method at 1200 °C for 5 h and sintered at 1500 °C for 10 h in air in a sacrificial powder bed consisting of BaCeO₃ and 10 wt% BaCO₃. The phase composition of the powders and ceramics was confirmed by X-ray diffraction (XRD) and scanning electron microscopy (SEM) combined with energy dispersive X-ray spectroscopy (EDS). The ceramics were polished down to 0.25 µm diamond suspension giving a smooth and flat surface. The average grain size was determined from SEM images using the linear intercept method.

The ¹³⁴BaO tracer source was deposited by drop casting of a barium nitrate solution on the surface of the host ceramics (BaTiO₃, BaZrO₃, BaCeO₃) followed by subsequent thermal annealing at 700 °C. The detailed description of the procedure is described in detail in a previous report.¹² The ¹³⁴BaO tracer layer where characterized by XRD and SEM/EDS. The coated pellets of the three materials were subjected to diffusion anneal at 1015–1200 °C for 2–90 h. The distribution of the isotopes ¹³⁴Ba and ¹³⁸Ba in the pellets after the thermal anneal was measured by secondary ion mass spectrometry (SIMS) using a Cameca IMS 4f instrument. The detailed description of the experimental conditions and optimization of the procedure is given elsewhere.¹²

III. RESULTS AND DISCUSSION

The microstructure of the three materials BaTiO₃, BaZrO₃ and BaCeO₃ are shown in Fig. 1A–C. The density of all the three sintered materials was higher than 97 % of theoretical density, and the crystal structure of the three materials, determined by XRD, were in good accord with literature.^{14,15} The average grain size of the BaTiO₃, BaCeO₃ and BaZrO₃ materials was 2.5±0.2, 5.4±0.1 and $1.1\pm0.1 \mu$ m, respectively. The microstructure of the homogenous film of ¹³⁴BaO deposited on one of the pellets is shown in Fig. 1D. The layer of ¹³⁴BaO covered completely the surface of the pellets. The amount of the solution deposited on each pellet corresponded to an average thickness of BaO of about 1 µm, and this was confirmed by SEM/EDS (not shown). The phase purity of the ¹³⁴BaO film was confirmed by XRD.

A typical ¹³⁴Ba diffusion profile in BaCeO₃ is shown in Fig. 1E. The diffusion profiles possess two regions with distinct slopes for all the samples investigated. The region close to the surface is dominated by lattice diffusion (Region I, Fig. 1E), while the part dominated by the grain boundary diffusion is located at a larger sputter depth (Region II, Fig. 1E). The penetration depth of the lattice diffusion was typically in the order of the average grain size or shorter. The lattice and grain boundary diffusion coefficients were determined by the fit to the experimental data using Fick's second law¹⁶ and Whipple-Le Clair's equation,¹⁷ as shown in the insets in Fig. 1E. The grain boundary transport occurred in the B-type kinetic regime where the condition $\delta < \sqrt{Dt} < d \text{ or } 1 < d/\sqrt{Dt}$ was fulfilled,¹¹ where *d* is the average grain size, δ is grain boundary width, *t* is time and *D* is diffusion coefficient.¹⁷

The lattice and grain boundary diffusion coefficients for the three materials are shown in Fig. 2 as a function of inverse temperature. The lattice diffusion coefficients were declining in the order $BaTiO_3$, $BaZrO_3$, $BaCeO_3$. The grain boundary diffusion coefficients were 4-5 orders of magnitude higher than the lattice diffusion coefficients for all the three materials, and were decreasing in the order $BaCeO_3$, $BaTiO_3$, $BaZrO_3$.



FIG. 1. The SEM micrographs of the A) $BaTiO_3$; B) $BaCeO_3$; C) $BaZrO_3$ microstructures of the sintered ceramics; D) BaO layer on the surface of the ceramics and E) SIMS depth profile of ^{134}Ba in $BaCeO_3$ after annealing at 1150 °C for 4 h, Insets: Regions of the profile used to determine lattice and grain boundary diffusion.



FIG. 2. The Arrhenius-type plot of 134 Ba lattice and grain boundary (GB) diffusion in BaTiO₃ (blue), BaZrO₃ (black) and BaCeO₃ (red). The error bars correspond to the standard deviation in fit to the SIMS profiles.

The diffusion coefficients for the three materials follow an Arrhenius behaviour and in general, the diffusion coefficient can be expressed by the Arrhenius equation (1),¹⁶

$$D = D_o \exp\left(-\frac{E_a}{RT}\right) \tag{1}$$

where, E_a is the activation energy, R is the gas constant, T is temperature and D_o is the pre-exponential factor. The temperature dependence of the lattice diffusion coefficients was fitted to equation (1) and the calculated activation energies for Ba²⁺ diffusion in BaMO₃ are plotted in Fig. 3 as a function of the size of the primitive cubic unit cell. The activation energy for Ba diffusion is decreasing with increasing size of the primitive unit cell.



FIG. 3. The activation energy for lattice diffusion of 134 Ba diffusion in BaMO₃ perovskites and the formation and migration entropies for Ba²⁺ cation vacancies plotted as a function of the unit cell volume per formula unit (f.u.).

Assuming that the diffusion mechanism involves a Ba²⁺ vacancy there are in principle two contributions to the activation energy, the enthalpy of formation of the Ba-vacancy, ΔH_f , and the enthalpy of migration of Ba²⁺, ΔH_m .¹² We first consider the enthalpy of formation of a Ba²⁺ vacancy. The most common point defects in perovskite materials are Schottky-type defects due to the considerably lower formation energies compared to Frenkel-type defects, which are less important in perovskite oxides.¹⁸ The Schottky defects is described by the defect equilibrium (2)

$$\operatorname{nill} \to \mathbf{v}_{Ba}^{\prime\prime} + \mathbf{v}_{M}^{\prime\prime\prime\prime} + 3\mathbf{v}_{O}^{\bullet\bullet} \tag{2}$$

where $v_{Ba}^{\prime\prime}$, $v_{M}^{\prime\prime\prime\prime}$ and $v_{O}^{\bullet\bullet}$ are Ba, M (=Ti, Zr, Ce) and O vacancies respectively. In BaMO₃ the partly Schottky defect equilibrium (3) is most likely dominant due to loss of BaO(g) during sintering,¹⁹

$$Ba_{Ba}^{x} + O_{O}^{x} \rightarrow v_{Ba}^{\prime\prime} + v_{O}^{\bullet\bullet} + BaO(g)$$
(3)

where Ba_{Ba}^{x} and O_{O}^{x} are Ba and O their respective lattice sites. Loss of BaO during sintering is well documented in case of BaZrO₃,⁷ and similar dominant point defects are anticipated in the two other materials BaCeO₃ and BaTiO₃ due to the high sintering temperatures applied. Based on first principles calculations the energy of formation for the partly Schottky-type defects, reaction (3), are 3.21, 2.80 and 2.58 eV for BaCeO₃, BaZrO₃ and BaTiO₃, respectively.^{18,20,21} The energy of formation is varying in the opposite manner compared to the experimental activation energy (Figure 3). The concentration of point defects in the ceramics is controlled by the sintering conditions, but annihilation of point defects may occur during cooling and subsequent annealing at temperatures below the sintering temperature. However, due to the low diffusivity of cations, the relaxation of the Schottky equilibrium (2), is rather slow and the cation point defect concentration can essentially be assumed to not be affected by the tracer annealing.²² We therefore suggest that the energy of formation of the Ba²⁺ vacancies does not contribute largely to the measured activation energy. Instead, we propose that the enthalpy of migration, ΔH_m is the dominating contribution to the experimental activation energy measured by tracer diffusion.

The migration path for Ba^{2+} via a Ba^{2+} vacancy is illustrated in Fig. 4. Here we only consider the simple cubic unit cell for $BaZrO_3$ since all the materials are cubic at high temperatures.^{15,23} Even though an M^{4+} -vacancy is closer as a neighbour to Ba^{2+} , the size and the energy of formation for such a vacancy are not favourable for Ba^{2+} to move through a M^{4+} vacancy.²⁰ We have recently reported excellent agreement between computed and experimentally determined activation energy for Ba^{2+} diffusion in $BaZrO_3$ by this diffusion mechanism.¹² If we now assume that the same diffusion path is likely for all three materials and that the experimental activation energy is dominated by ΔH_m , the decreasing activation energy in the order $BaTiO_3$, $BaZrO_3$, $BaCeO_3$ can be correlated with the size of the primitive unit cell. While the jumping distance will increase with size, the energy of



FIG. 4. A schematic of the Ba^{2+} (green) diffusion pathway via a Ba^{2+} vacancy in nonstoichiometric cubic $BaMO_3$. Yellow – M cation, red – oxygen (ion size mismatch is neglected for simplicity).

the intermediate transition state is expected to decrease as the distance to M^{4+} becomes larger with increasing size of the unit cell. We therefore propose that the activation energy for Ba^{2+} diffusion measured by tracer diffusion experiments is reflecting the decreasing activation barrier for Ba^{2+} diffusion in the order BaTiO₃, BaZrO₃, BaCeO₃. The energy barrier for A-site diffusion has recently been discussed for (Ba,Sr)ZrO₃ materials.¹³

The pre-exponential factor D_o in equation (2) can be expanded as equation (4),²⁴

$$D_o = \lambda^2 \eta \exp\left(\frac{S_f + S_m}{k_B}\right) \tag{4}$$

where, k_B is a Boltzmann constant, λ is the jump distance, η is the vibration frequency and S_f and S_m are the formation and migration entropies for Ba²⁺ cation vacancies, respectively. A similar analysis of the pre-exponential factor have previously been applied to tracer diffusion of Zr⁴⁺ in ZrO₂ materials.²⁴ D_o for Ba²⁺ lattice diffusion in the three materials was determined by the fit to the data of the Arrhenius plots in Fig. 2. $S_f + S_m$ calculated using equation (4) is also included in Fig. 3. λ was calculated from the unit cell of the three materials, while η was estimated from the Debye temperature θ_D , $\eta = \theta k/h$, where k and h are the Boltzmann and Plank constants, respectively. The estimated entropy using data reported for the materials is declining with increasing size of the unit cell, see Fig. 3. Following the argumentation related to the activation energy, the entropy term in equation (4) is dominated by the entropy of migration, S_m . The increasing size of the unit cell and thereby longer bonding distances in the series BaTiO₃, BaZrO₃, BaCeO₃ reduce both the enthalpy and entropy of migration.

Finally, the activation energy for the grain boundary diffusion was determined to be 248±70, 303±49 and 256±59 kJ/mol for BaTiO₃, BaZrO₃, and BaCeO₃, respectively. Considerably faster diffusion along grain boundaries has been reported for several oxide materials including perovskites and fluorites.¹² The activation energy for cation diffusion along grain boundaries is lower compared to the diffusion through the lattice probably due to a higher defect concentration giving more space and longer distance between A–A or A–M, which reduce Coulomb's potential and the energy barrier for the cations to diffuse along the grain boundaries.

The activation energy for lattice cation diffusion for the three materials confirms that the activation barrier is reduced with increasing size of the M-cations and hence the unit cell volume. A similar trend has also been reported for spinel-type ferrite compounds.²⁵ A recent computational study has shown that the energy barrier of A-site cation diffusion in (Ba,Sr)ZrO₃ is dependent on the intermediate configurations during diffusion of the A-cation to the next A-site vacancy and is inversely proportional to the unit cell volume.¹³ This can be attributed to Coulomb's repulsion of positively charged species either A–A or A–B in ABO₃. The increased B cation size or expanded lattice consequently increases

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the distance between two cations and reduces the Coulomb's potential in the energy barrier for A-cation to diffuse. The barrier of A-site diffusion is dependent on A- and B-site interaction and charge of the cation. The stronger the repulsion between the A and B sites, the higher the energy barrier for migration of the A-site cation.¹³

The Ba lattice diffusion in BaMO₃ compared to the A-site cation diffusion in general in perovskites reported in the literature revealed no apparent trend.^{26–38} In addition, the diffusion mechanisms for the data reported in the literature are usually not described. The point defect chemistry after materials processing determines the dominating diffusion mechanism as shown for BaZrO₃.¹² The A-site diffusion in A^{II}B^{IV}O₃ perovskites is accompanied with higher activation energies compared to diffusion in A^{III}B^{III}O₃ perovskites. The size, charge of the cations, tolerance factor and structural distortions of the perovskite lattice, influence the activation energy for diffusion.

As a consequence, the fast A-site diffusivity with low activation energy could be disputed in relation to the AO segregation on the surface of the alkaline earth element containing materials, such as $SrTi_{1-x}Fe_xO_3$ and $La_{1-x}Sr_xCo_{0.2}Fe_{0.8}O_{3-\delta}$.^{39,40} The high processing temperature and segregation of BaO as BaCO₃ give rise to an interesting defect chemistry as discussed for BaZrO₃ with respect to materials stability and Ba-mobility.⁷ Novel behavior with the implication to cation intermixing has been observed at the interface of LaAlO₃/SrTiO₃ heterostructures such as two dimensional metallic conductivity, magnetic scattering and superconductivity.⁴¹

IV. CONCLUSION

In summary, we investigated and compared the tracer diffusion of 134 Ba in BaMO₃ (M = Ti, Zr, Ce). It was demonstrated that the lattice diffusion coefficient of Ba²⁺ in BaMO₃ perovskites is inversely proportional to the size of the M-cation. The activation energy of Ba²⁺ lattice diffusion in BaTiO₃, BaZrO₃ and BaCeO₃ was measured to be 442±62, 395±44 and 349±23 kJ/mol, respectively. The diffusion mechanism for Ba²⁺ was proposed to perceive via Ba²⁺ vacancies. The enthalpy and entropy of migration of Ba²⁺ decreased in the order BaTiO₃, BaZrO₃ and BaCeO₃.

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