Role of Diffusion Phenomena in the Processing of Ceramics

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The role of diffusion in ceramic processing is discussed. The utility of secondary ion mass spectroscopy (SIMS) is highlighted for the evaluation of diffusion coefficients in ceramic materials. By comparing diffusion coefficients obtained in this manner with those obtained indirectly from creep measurements, we identified the ion species that govern creep in yttrium aluminum garnet (YAG) ceramics and we showed that diffusion involving metastable defects plays an important role in ceramic processes such as sintering. The oxygen diffusion coefficients of thin films were evaluated, and the defects involved were shown to be metastable, and their origins were clarified. Furthermore, their relationship with reactivity was discussed in thin films.

Key-words: Diffusion, Defect, Garnet, Zinc oxide, Oxygen, SIMS, Creep, Thin film

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1. Role of diffusion in inorganic materials

There are basically two reasons for studying the diffusion in solids.

One is to obtain basic information relating to crystal lattice defects. Crystal lattice defects can be zero-dimensional point defects, one-dimensional line defects such as dislocations, two-dimensional plane defects such as grain boundaries, and three-dimensional defects such as voids formed by the aggregation of other defects. But instead of existing purely as separate entities, these different types of defect generally interact with each other. These interactions are often mediated by point defects at the lowermost level of the defect hierarchy. The development of techniques such as TEM has made it relatively easy to observe material structures at atomic scales — such as dislocations and higher-order defects — and to follow their kinetic behavior. However, techniques such as TEM are generally unable to evaluate the concentration or motion of point defects which determine the behavior of higher-order defects. Since the kinetic behavior and concentration of point defects are linked by a direct theoretical relationship to the diffusion coefficient, the measurement of diffusion in solids is regarded as a useful tool for studying point defects.

As the second case in point, the study of diffusion helps us to understand some reactions in solids. For example, when new phases are formed by solid-phase reactions to which no contribution is made by liquid or gas phases, the process is governed either by the reactions at interfaces or by the diffusion of constituent ions or atoms. In solid-phase reactions, the former is usually overwhelming faster and as a result it is necessary to know the diffusion coefficient in order to understand the reaction rate in detail.

In this paper, based on our research results obtained for such purposes, I briefly discuss diffusion phenomena and methods for evaluating them, and I explain the relationship between sintering, creep phenomena and diffusion—which is of considerable concern in ceramic material fabrication. Metastable point defects, which play an important role in thin films, are also described.

2. Methods for evaluating diffusion coefficients

Solid-state diffusion in ceramics can be regarded as a process whereby the diffusing species moves closer to a homogeneous or equilibrium state. In many real materials — glass being a typical example — the existence of metastable states is inevitable. Although glass is thermodynamically unstable, it appears stable. One of the reasons is that the diffusion coefficient is too low to form a crystalline precipitate in the glass phase. An indicator of a material’s propensity to move towards equilibrium with time is its diffusion coefficient $D$. In this paper I will refer to various types of diffusion coefficient which are normally differentiation by adding subscripts to $D$.

Solid-state diffusion phenomena are modeled based on Fick’s first and second laws. The flux $J$ of a diffusing species flowing per unit area is expressed as follows:  

$$J = -D \frac{dc}{dx}.$$  \hspace{1cm} (1)

where $c$ is the concentration of the diffusing species, and $x$ is the distance in the flux direction. Equation (1) is equivalent to saying that the magnitude of the diffusion flux is proportional to the concentration gradient, where the diffusion coefficient $D$ is a proportional coefficient. Equation (1) is called Fick’s first law, and is often applied to steady-state phenomena where the concentration does not change with time. Fick’s second law is qualitatively formulated as follows, and is applied to diffusion phenomena that are nonsteady state.

$$\frac{dc}{dt} = D \nabla^2 c$$  \hspace{1cm} (2)

If Eq. (2) is solved under certain boundary conditions, it is possible to determine the concentration at any position at a certain specified time, even in nonsteady-state cases.\(^{3,4}\) Two useful solutions of this equation are presented here. One is the solution for a thin-film diffusion source, which is given by the following formula:

$$c = \frac{\alpha}{2 \sqrt{\pi Dt}} \exp \left( -\frac{x^2}{4Dt} \right).$$  \hspace{1cm} (3)

This is used in cases where a quantity $\alpha$ of the diffusing species is uniformly applied as a thin coating to the surface of a solid material and allowed to diffuse into it. Here, the thickness of this uniform coating is assumed to be negligible for practical purposes.
Next is the case where the concentration of the diffusing species at the surface of a semi-infinite medium is constant, and is given by $c_1$. In other words,

\[
\begin{align*}
  c(x, 0) &= c_0 \quad (x > 0, t = 0) \\
  c(0, t) &= c_1 \quad (\forall t, x = 0)
\end{align*}
\]

In this case, the concentration $c(x, t)$ at a certain time $t$ and position $x$ is given by the following formula:

\[
\frac{c(x, t) - c_1}{c_0 - c_1} = \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right).
\]

(4)

where "erf" denotes the error function. This solution is useful for modeling situations such as diffusion between two materials having limited solid solubility. Also, although the diffusion coefficient of oxygen in ceramics is normally derived by a method known as gas phase-solid phase substitution,\(^6\) Eq. (4) often appears in the analysis of this mechanism.

There are numerous ways of measuring diffusion coefficients, but they can be broadly divided into two types. One involves measuring the diffusion profile of the diffusing species and obtaining the diffusion coefficient by mapping the results to the solution of a suitable diffusion model. Another approach currently in use is based on the fact that the diffusion coefficient is proportional to the vibration frequency of the diffusing species. Table 1 lists the principal methods for evaluating the types of diffusion that belong in these categories.

So far we have discussed diffusion within crystal lattices via vacancies and interstitial mechanisms, i.e., volumetric diffusion. However, real solids typically include other types of defect besides point defects. For example, dislocations are always present at the surface to some extent. The material may also consist of crystal grains instead of a single crystal, and unless the material is pure it may also contain two-phase boundaries. It is easy to see how the diffusing species can jump more frequently along the cores of dislocations, along grain boundaries and across the surface than within the bulk lattice, and in practice these effects are often of great importance.\(^6\)

Since locations such as these have high diffusion coefficients, they are called high-diffusivity paths. Here we will discuss diffusion at grain boundaries, which is the most typical of high-diffusivity paths. The surfaces of ceramics can also be treated as a type of grain boundary, and a similar solution method can also be employed for dislocations. Grain boundary diffusion is modeled based on the diffusion model shown in Fig. 1. This was first attempted by Fisher,\(^7\) but these days diffusion is more commonly analyzed using LeClaire's formula\(^8\) (shown below) which can be formulated even with large numbers of boundary conditions.

\[
D_{gb} \cdot \delta = 0.66 \left( \frac{4D_k}{l} \right)^{1/2} \left[ -\frac{\partial \ln c}{\partial x^2} \right]^{-5/3}
\]

(5)

In this formula, it should be pointed out that $D_{gb}$ is not determined as an isolated term, but is normally only obtained as the value of its product $D_{gb} \cdot \delta$ with the grain thickness $\delta$. From this ratio, $\delta$ is found to be of the order of 1 nm in most metallic materials. There are few examples of direct comparisons with ceramics, but a value for $\delta$ of the order of 1 nm was reported by Atkinson for the diffusion of Ni ions in NiO.\(^9\) and it seems that solid-state materials all exhibit values of roughly the same order. Based on observations of the vicinity of grain boundaries using electron microscopes, this value seems to be appropriate since hardly any grain boundary disorder is observed at directly bonded grain boundaries when there is no grain boundary phase.

### Table 1. Measurement Range of Diffusion Coefficients When Using Various Diffusion Coefficient Measurement Methods

<table>
<thead>
<tr>
<th>Method</th>
<th>Grind thickness, $\Delta x$</th>
<th>Range of diffusion coefficients $(\text{cm}^2/\text{s})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct method*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mechanical grinding</td>
<td>$5\mu m$</td>
<td>$10^{15}$-$10^9$</td>
</tr>
<tr>
<td>Microtome</td>
<td>1-100 $\mu m$</td>
<td>$10^{13}$-$10^6$</td>
</tr>
<tr>
<td>Chemical etching</td>
<td>$10 \mu m$</td>
<td>$10^{11}$-$10^9$</td>
</tr>
<tr>
<td>Electrochemical etching</td>
<td>$50nm$</td>
<td>$10^{10}$-$10^8$</td>
</tr>
<tr>
<td>SIMS</td>
<td>1-10nm</td>
<td>$10^{12}$-$10^9$</td>
</tr>
<tr>
<td>XMA(EPMA)</td>
<td>$2 \mu m$</td>
<td>$10^{10}$-$10^9$</td>
</tr>
<tr>
<td>RBS</td>
<td>$50 \mu m$</td>
<td>$10^{10}$-$10^9$</td>
</tr>
<tr>
<td>Nuclear reaction</td>
<td>20-100nm</td>
<td>$10^{13}$-$10^9$</td>
</tr>
<tr>
<td>Indirect method</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NMR</td>
<td></td>
<td>$10^{16}$-$10^9$</td>
</tr>
<tr>
<td>Neutron scattering</td>
<td></td>
<td>$10^9$-$10^8$</td>
</tr>
<tr>
<td>Moessbauer spectroscopy</td>
<td></td>
<td>$10^{10}$-$10^7$</td>
</tr>
<tr>
<td>Ionic conductivity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Resistance</td>
<td></td>
<td>$10^{16}$-$10^9$</td>
</tr>
<tr>
<td>Magnetic anisotropy</td>
<td></td>
<td>$10^{15}$-$10^9$</td>
</tr>
</tbody>
</table>

*Range of diffusion coefficients is calculated under the condition of 1/100 of surface concentration at 10 $\Delta x$ after diffusion annealing duration for $10^3$-$10^9$ seconds.
Fig. 1. Grain boundary diffusion model. Parts that are distant from the grain boundaries are less affected by grain boundary diffusion. The diffusion profile near the surface can mostly be explained by lattice diffusion. When there is pronounced grain boundary diffusion, the diffusing species diffuses by lattice diffusion into the grains from the grain boundaries in deep parts.

Fig. 2. Three-dimensional distribution of the oxygen isotope \( ^{16}\text{O} \) after diffusing into a polycrystalline zinc oxide ceramic.\(^{10}\) The isotope diffuses by a volume (lattice) diffusion mechanism close to the surface, but diffusion along grain boundaries occurs preferentially in deep regions. This grain boundary diffusion plays a decisive role in the functional expression of grain boundary phenomena such as in varistors. The model depicted in Fig. 1 is reproduced.

Fig. 3. NanoSIMS measurement of the Si distribution in a transparent YAG sintered ceramic (total quantity: 700 ppm).

(a) Sample with a stoichiometric composition \( (Y/Al = 3/5) \). Although Si segregates toward the grain boundaries, it also forms a solid solution of the order of about 700 ppm inside the grains.

(b) Sample with a 1% excess of Y. The heterogeneity functions as Si scavenger, and not only clears up the grain boundaries but also reduces the Si concentration inside the grains less than 5 ppm.

Fig. 4. Transparent YAG sintered ceramics obtained by the urea method\(^{13-15}\) (provided by Konoshima Chemical Co., Ltd.).

(a) Ce-doped sample (50 mm diameter, 5 mm thickness).

(b) Dy-doped sample (10 mm diameter, 12 mm thickness).

analyzed by techniques such as XMA and SAM, the practical detection limit of such techniques is of the order of a few percents. Here, the defect structure resulting from the diffusion of impurities is completely different from the state before diffusion which we want to evaluate. Figure 2 shows a typical example of the three-dimensional distribution of oxygen-18 that has diffused into zinc oxide ceramics. This figure clearly illustrates the preferential diffusion of oxygen along grain boundaries.\(^{10}\) It should be pointed out that the parts where grain boundary diffusion appears to be taking place actually show the traces of oxygen-18 that have diffused by lattice diffusion from the grain boundaries toward the interior of the grains.

Although SIMS has a good resolution in the depth direction, its planar resolution has remained on the order of microns in conventional equipment. Since ceramics with micron or sub-micron grain sizes are becoming increasingly commonplace, there is a growing need for improved planar resolution. By adapting the primary ion beam system, Slodzian et al. have developed a device with improved planar resolution to 30–50 nm without impairing the sensitivity.\(^{11}\) Figure 3 shows the distribution of Si in YAG transparent polycrystalline ceramics evaluated using this device. The distribution in Fig. 3(b) is for a ceramic with a roughly stoichiometric composition, while that in Fig. 3(a) corresponds to a composition with a slight excess of yttrium (from 500 to 3000 ppm). As this figure clearly shows, the phase containing excess yttrium behaves as a scavenger that clears up not only the grain boundaries but also inside the grains. As these two examples show, SIMS is a very useful tool for research in diffusion.
4. Processes contributed by diffusion

Creep and sintering

The evaluation of diffusion rates based on creep measurements involves using a fully sintered solid sample, in which the amount of defects is considered to be more or less equal to that of a sample used to evaluate diffusion coefficients, and it is thought that the diffusion coefficients obtained from the analysis of creep data and diffusion coefficients that have been measured directly relatively matched. Solid-state creep deformation depends on the stress $\sigma$, crystal grain size $d$ and temperature $T$. The region in which the deformation rate is constant with time is referred to as steady-state creep.

The mechanism in this region has been studied in considerable detail, and experimentally it is generally expressed by Dorn’s formula\(^5\) as shown below:

$$\dot{\epsilon} = A \frac{G^6 D_c}{kT} \left( \frac{\sigma}{G} \right)^n \left( \frac{d}{\bar{d}} \right)^m \quad (6)$$

Here, $D_c$ is the diffusion coefficient that contributes to creep deformation, $G$, the modulus of rigidity, $\bar{d}$, the Burgers vector, $k$, the Boltzmann constant, $T$, the temperature, and $A$, an experimentally determined constant. The indices $m$ and $n$ are called the grain size index and stress index, respectively, and have values that are dependent on the creep deformation mechanism. The term $D_c$ depends on the rate-governing mechanism. Creep deformation mechanisms include dislocation creep inside grains, grain boundary creep, diffusional creep and superplasticity creep. These mechanisms have been the subject of many theoretical studies, and for each mechanism the values of $m$ and $n$ and the type of temperature-dependent activation energy $AH$ have been shown. It should be pointed out that the diffusion coefficients are linked in all of these mechanisms. In particular, the diffusion coefficient changes by one order of magnitude with changes in temperature in this formula, and thus it is safe to say that creep deformation is governed by diffusion.

The relationship between diffusion and creep in ceramic solids is described, based on some examples of yttrium–aluminum–garnet (YAG) sintered ceramics that we have fabricated. Since YAG has a crystal structure belonging to the cubic system, it exhibits isotropic properties when formed into a polycrystalline ceramic. In this respect it differs significantly from materials with anisotropic crystal structures, such as alumina. We used the area method to produce powders with excellent sintering properties, from which we made the transparent sintered ceramics shown in Fig. 4.\(^{13}\) Since it was first shown that sintered ceramics doped with rare-earth elements such as Nd can function as ceramic lasers,\(^{14,15}\) many attempts have been made to produce YAG ceramic lasers.\(^{16,17}\) Also, since these materials exhibit superior linear transmittivity and chemical stability, they are useful for HID lamp tubes. For applications such as lasers and lamp tubes, the mechanical properties of these materials are of key importance. We have studied their fracture property and creep behavior, and as a result we have shown that even in small quantities Si ions and their distribution play crucial roles in determining these characteristics. This analysis was helped considerably by the SIMS analysis results shown in Fig. 3, which shows the relationship between diffusion and creep using the same material.

In crystallographic terms, YAG basically consists of oxide ions and cations having 4-, 6- and 8-coordinate positions, and yttrium is situated at the 8-coordinate position. Each of these ions has a different diffusion coefficient, so it is important to consider which of these ions governs the creep rate. In experiments using actual SIMS measurements, since both aluminum and yttrium have only one stable isotope, the aluminum was substituted with gallium and the yttrium was substituted with ytterbium, and experimentation was performed with a very small quantity of diffusing species.\(^{18}\) Figure 5 shows an example of the SIMS diffusion profile. The contribution of volume diffusion near the surface is divided into a main part and a part related to internal grain boundary diffusion. We used Eqs. (3) and (4) to determine the volume diffusion coefficients for positive ions and oxide ions, respectively,\(^{19}\) and for the grain boundary diffusion we used Eq. (6) to obtain the product of the grain boundary thickness $d$ and the grain boundary diffusion coefficient $D_b$. Figure 6 shows the temperature dependence of each of the diffusion coefficients. This result shows that the aluminum ions diffuse much faster than the yttrium ions, while oxide has an intermediate value between them.

Figure 7 shows the diffusion coefficients determined from the creep rate of YAG.\(^{20}\) Since ceramic materials consist of at least two elements, there is always the issue of which element’s diffusion controls the phenomenon. In creep and sintering processes whose mechanisms are governed by diffusion, the rate of the process is controlled by the diffusion of the slower diffusing species. In the figure the volume diffusion coefficient and grain boundary diffusion coefficient of the above-mentioned positive ions\(^{18}\) are shown together. When the diffusion rate based on the creep rate is assumed to be the volume diffusion rate, it has a value close to that of the cations, which shows that the creep of YAG is governed by the volume diffusion of cations.

Sintering is another process that is governed by diffusion.\(^{21}\) Numerous researchers have proposed a variety of sintering mechanisms in which solid phases participate, but in most cases the diffusion coefficients are expressed as formulae and vary differently with temperature depending on the attributes of the diffusing species. However, in many cases the actual diffusion coefficients do not agree with the diffusion coefficients derived from the results of sintering experiments. This is because when sintering ceramics it is common practice to use an activating powder such as an ultranine powder in the precursor materials, whereas single crystals or polycrystalline materials that have already been sintered are used to measure the diffusion coefficients. As a result, their values do not necessarily match that of the ac-
Fig. 6. Diffusion coefficients in YAG as determined by SIMS.
(a) Volume diffusion coefficient \(D_v\) of Yb ions in YAG (diffusion via yttrium sites). YAGPS, YAGPY and YAGS, respectively, represent the volume diffusion coefficients of a stoichiometric transparent sintered ceramic, a transparent sintered ceramic with a 1% excess of Y, and a single crystal.
(b) Temperature dependence of the product \(\delta \cdot D_v\) of the grain boundary diffusion coefficient of Yb ions in YAG \((D_g)\) and the grain boundary thickness \(\delta\). YAGPS and YAGPY, respectively, represent the values for a stoichiometric transparent polycrystalline ceramic and a transparent polycrystalline ceramic with a 1% excess of Y. (N.B.: Since these values are multiplied by \(\delta\), they are expressed in units of \(\text{cm}^2\cdot\text{s}^{-1}\).)
(c) Temperature dependence of the volume diffusion coefficients for each type of site in a stoichiometric transparent YAG sintered ceramic.
(Key: ----- = yttrium sites; ------ = aluminum sites; ----- = oxygen sites.)

Fig. 7. Comparison of YAG creep analysis results and diffusion coefficients.
(a) Results of creep analysis using Dorn’s formula. Variation of the stress- and grain-size-compensated strain rate \((=AD_e\), see Eq. (6) of text) with \(1/T\) for single-crystal and polycrystalline \((m = 0, n = 1)\) YAG. Good agreement between the different data sets is apparent; creep activation energy is identical \((Q_c = 590 \text{ kJ/mol})\) for single crystals and polycrystals.
(b) Comparison of diffusion coefficients.
The creep data shown by the dashed line was determined by assuming the distortion rate to be \(D_e\), when the rate is governed by volumetric diffusion and \(D_g\) when it depends on volumetric diffusion. The values of the volumetric diffusion coefficient \(D_v\) and grain boundary diffusion coefficient \(D_g\) at yttrium sites as shown by the solid line correspond to the data shown in Figs. 6(a) and (b), respectively, except that in this case it was assumed that \(\delta = 1 \text{ nm}\).

tivating powder. In other words, the activating powder includes a large quantity of metastable defects, and it is necessary to perform experiments that take these metastable defects into account.

The authors have proposed a method for determining the diffusion coefficient of this sort of powdered material. The results of this method are shown in Fig. 8, and are clearly different from those of a single crystal. On the other hand, Shirasaki et al. have proposed a method for evaluating the diffusion coefficient in the intermediate stage of sintering.
Shirasaki, Ikuesue et al. reported on the comparison of diffusion coefficients obtained by this method during sintering
with diffusion coefficients obtained from sintered ceramics, and obtained an excellent agreement as shown in Fig. 9.44

As described above, it has become clear that diffusion via metastable defects often governs the reactions involved in
ceramic processes.

5. Thin film processing and diffusion

In the previous section it is shown that the presence of metastable defects and diffusion associated with these
defects are key factors in important ceramic processes such as sintering. On the other hand, since thin film processing
mostly involves nonequilibrium processes, it is predicted that large quantities of metastable point defects are intro-
duced during processing. We have studied how defects introduced during processing affect the physical properties.
Here the importance of metastable defects is also shown by discussing the metastable nature of thin films formed by RF
sputtering.

Figure 10 shows cross-sectional TEM photographs of a calcium titanate film deposited by sputtering. This film was
deposited on a single crystal of strontium titanate. As shown in the low magnification TEM photograph, there are many
subgrain boundaries due to lattice misfit. However, at higher magnification the lattice structure does not appear to be
so disordered, and a continuous lattice is formed with the strontium titanate substrate. On the other hand, as the ratio
of titanium to calcium is varied, the lattice constant is found to vary continuously up to Ca/Ti = 0.9–1.1, and absolutely
no secondary phase is observed. However, in the bulk material this solid solution range is only permitted to be
300–500 ppm, and the wide solid solution range in thin films shows that the thin films are in a nonequilibrium state.
Although this kind of discrepancy of the composition in strontium titanate and barium titanate is eliminated by the
formation of planar defects that are clearly visible in TEM

Fig. 8. Oxygen ion diffusion coefficients in powder, polycrystal-
line and single-crystal MgO as a function of the reciprocal tem-
perature.
1: single crystal;2) 2: single crystal; 3: sintered at 1723 K;4) 4: sintered at 1473 K;5) 5: single crystal; 6: powder sample decom-
posed at 1423 K;7: powder sample decomposed at 1173 K. Since the sample decomposed at 1173 K has a larger diffusion
coefficient than the other samples, it thus follows that the activity is
maintained by the introduction of a large number of metastable oxy-
gen defects.

Fig. 9. Comparison of diffusion coefficients determined from sintering and the diffusion coefficient of 16O.
(a) Values for easily sintered MgO and hard-to-sinter MgO. The diffusion coefficient of sintering is the value determined by Bannister’s
formula.41 Since there are no differences in activation energy, it follows that the sintering mechanisms are the same, but the diffusion
coefficients are different. A close match with the diffusion coefficient of the isotope is obtained.
(b) Comparison of the diffusion coefficient obtained from the sintering of alumina with the value obtained with diffusion of an isotope. The
two values match perfectly, and this data shows that the sintering rate of alumina is governed by the volumetric diffusion of oxygen.
observations, the calcium titanate thin films are characterized in that no pronounced defects can be seen.

If we assume that compositional discrepancies are due to ionic vacancies, then it follows that ionic vacancies are present at both sites in compositions with excess calcium and excess titanium.

Ca-excess composition: \( \text{Ca}_{1+x} \text{Ti}_x \text{V}_{3-x} \text{O}_{3+\delta} \)  
Ti-excess composition: \( \text{Ca}_x \text{V}_{\text{Ca}_x \text{Ti}_{1-x}} \text{O}_{3+\delta} \) \( V^{\delta+} \) (7)

Another characterizing feature is that oxygen vacancies are present in both types of composition (excess Ca or excess Ti). This suggests that the oxygen diffusion coefficient increases when the composition is shifted either way. Figure 11 shows the results of evaluating the oxygen diffusion together with that of a single crystal. Although the single crystal also have some degree of compositional shift, this should remain within 300 ppm reflecting the bulk characteristics. Meanwhile, the thin film sample exhibits an oxygen diffusion coefficient two orders of magnitude larger than that of a single crystal of the same material, clearly demonstrating the presence of metastable oxygen vacancies. Figure 12 shows how the oxygen diffusion coefficient varies with the Ca/Ti ratio in a thin film of calcium titanate.

In annealed samples, the smallest diffusion coefficients are obtained in compositions close to cation stoichiometric, and the discrepancy in the composition shown in Eq. (7) constitutes the cause of metastable oxygen vacancies.

On the other hand, the diffusion coefficient decreases closer to equilibrium as the material becomes fully annealed as shown in Fig. 13. However, since heterogeneity is also observed in these annealed crystals, a compositional offset still exists, as does a corresponding quantity of defects. The metastable oxygen vacancies that are reduced by annealing show that metastable point defects other than defects arising from the composition discrepancy are present in the thin film. Oxygen vacancies are generally thought to occur in the following two ways:

\[ \text{O}_2^\cdot \rightarrow \text{V}_0^\cdot + 1/2 \text{O}_2 \]
\[ \text{null} \rightarrow \text{V}_\text{Ca}^\cdot + \text{V}_{\text{Ti}}^\cdot + 3\text{V}_\text{O}^\cdot \]  

(8)

The upper part of Eq. (8) represents the partial reduction of the lattice, and the lower part represents the introduction of metastable vacancies with a Schottky profile. If the above assumption is correct, then metastable oxygen vacancies should be present even in monoxides, such as zinc oxide, where there is no composition discrepancy of cations.

Fig. 10. TEM photographs of a perovskite calcium titanate film formed by RF sputtering on a single-crystal \( \text{SrTiO}_3 \) substrate.  
(a) Low magnification. The deposited film has columnar structures with a diameter of 50–100 nm.  
(b) High magnification lattice image. There are no visible planar defects caused by the change in composition. The deposited film is well matched to the substrate, and we confirmed that it is continuously joined to the \( \text{SrTiO}_3 \) lattice of the substrate.

Fig. 11. Temperature dependence of the oxygen ion diffusion coefficient in calcium titanate. The film deposited at room temperature is amorphous, while the film deposited at 873 K has a perovskite structure as shown in Fig. 10. However, both samples have larger diffusion coefficients than that of a single crystal due to the metastable properties.

Fig. 12. Preannealing temperature dependence of oxygen diffusion coefficient in a thin film of calcium titanate. This figure shows the results of pre-annealing for 10 hours at a prescribed temperature before diffusion annealing at a temperature of 853 K (- - - -). The extrapolated values for a single crystal at 853 K are also shown for comparison (-----). As the pre-annealing temperature increases, the metastable properties decrease, but after 1100 K it increases again due to the effects of positive ion diffusion from the substrate. Note that this matches the values obtained with a single-crystal sample.
Fig. 13. Composition dependence of the oxygen diffusion coefficient in a strontium titanate thin film.
In non-annealed samples the diffusion coefficient increases with the value of (Ca/Ti), but in pre-annealed samples it takes the smallest value in samples close to stoichiometric compositions. In other words, in pre-annealed samples the metastable properties become stronger the more the composition ratio is shifted.

Fig. 14. Oxygen diffusion coefficients in zinc oxide thin films.29 In an unprocessed thin film, the value is 3-4 orders of magnitude larger than the extrapolated value for a bulk sample. Sintering brings the value closer to that of a bulk sample. Since this reduction is associated with a reduction in electrical conductivity, it suggests that the defects that contribute to conduction are metastable oxygen defects.

Figure 14 shows the results of measuring the volumetric diffusion of oxygen in a film of zinc oxide formed by sputtering on single-crystal alumina.29 As mentioned already, the volume diffusion of oxygen in zinc oxide varies with the impurity concentration in the extrinsic region, even at equilibrium,10 but in a thin film the oxygen diffusion coefficient becomes approximately 4 orders of magnitude larger than in the bulk material, which does not reflect a difference in impurities. In other words, it corresponds to the introduction of metastable defects. Since these vacancies are greatly reduced by annealing in an oxidizing atmosphere, they are thought to be oxygen vacancies produced by the mechanism of the top part of Eq. (8). The electrical conductivity of these zinc oxide thin films is markedly reduced by annealing in an oxidizing atmosphere.29 The above phenomena suggest that metastable oxygen vacancies in thin films act as donors.

The above-mentioned increase in diffusion coefficient by metastable oxygen vacancies is also expected to be accelerated by reactions inside the solid. We used this high activity to improve the crystallinity of a zinc oxide-based homologous phase thin-film (InO2(ZnO)12). Since this compound has a layered structure, it is expected to have two-dimensional properties, but for this purpose it is important to maintain a superior layered structure. Figure 15 shows a film grown under more or less the same conditions as the zinc oxide thin film. This film does not exhibit adequate crystalline properties. Therefore, after preforming zinc oxide and homologous layers several tens of nm thick, these layers were fully annealed at a low temperature of approximately 400 degrees to form a homologous phase film, whereupon a film with superior crystalline properties was obtained.30-32 We called the initial layer a self-buffer layer, and it seems that the essential point is that it was possible to use the high activity of the thin film to recrystallize the buffer layer to a high degree.

6. Conclusion

Experimental techniques for analyzing diffusion in solids were established in the latter half of the twentieth century. It has to be said that they are still inadequate for analyzing fine (micron and submicron) structures or metastable configurations. In this paper — focusing on the diffusion coefficients of ceramics — we have briefly discussed the techniques available for measuring and exploiting this diffusion...
sion, and we have demonstrated the existence and importance of metastable defects. Of course, this paper has not dealt with all forms of diffusion. It is difficult to directly inspect the mechanisms in experimental diffusion coefficient measurements, and it is necessary to interpret the results of such experiments alongside the predictions of theoretical studies. For example, in a maximally packed oxygen sublattice, it has simply been assumed that it is difficult for interstitial ions to make any sort of contribution due to this maximal packing. However, theoretical calculations have shown that—despite appearances—it is possible for interstitial ions to exist under such circumstances. It is therefore necessary to review these diffusion mechanisms, even in materials such as MgO. This review can be implemented based on the classical lattice dynamics of Mott–Littleton, although rapid progress is being made by a general-purpose software package developed by Nogrette et al. 13

Furthermore, it is thought that a molecular dynamic approach is effective for analyzing structures close to grain boundaries, which have an important bearing on the clarification of grain boundary diffusion phenomena. However, it should be pointed out that these classical theoretical calculations also have problems. For example, classical calculations use various empirical potentials, but there are cases where completely opposite conclusions can be reached depending on which of these is used. "Ab initio" calculations should also be incorporated in order to overcome this drawback.

References

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