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Effect of impurities on the diffusion-controlled creep activation energy in MgO

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By studying the theoretical variation of mass-transport self-diffusion activation energy, with temperature and vacancy concentration, the various rate-limiting possibilities for diffusional creep in MgO are discussed. Because of anion–cation ambipolar coupling it is shown that only four distinct regimes of diffusion controlled creep are, in principle, observable in MgO when considering lattice diffusion. As oxygen ions are by far the slowest species a minimum in the activation energy appears at some temperature for an oxygen vacancy excess but correlatively for a magnesium vacancy excess such a minimum should not be observed. The analysis of creep energies in the experimental domain investigated by several authors allows, in the first case, a correlation with the extrinsic diffusion of oxygen vacancies in excess, but in the reverse case of magnesium vacancy excess no such correlation is observed with extrinsic diffusion of rarefield oxygen vacancies. Instead, neutral vacancy pairs should prevail in the diffusional creep of MgO in this case.

1. Introduction

In the creep of ionic solids at high temperature the creep rate is frequently limited by a process in which the rate-controlling step of deformation involves the diffusive transfer of vacancies from sources to sinks (e.g. dislocations, grain boundaries). In the case of those crystals which contain two components, the steady-state creep rate is tentatively correlated with the activation energy for self-diffusion of the slower diffusing ion. This correlation is not well established for MgO since, among the large number of creep data currently available on both the single crystal and polycrystalline form, a wide variety of creep activation energies have been reported. This results, in part, from wide differences in the microstructures, such as grain sizes, and from the possibility of multiple transport paths such as grain-boundary diffusion, pipe diffusion or lattice diffusion. Moreover, impurities in MgO play a significant role in creep experiments, where observed activation energies for a given mechanism are not unique but are known to vary with extrinsic material characteristic, as well as in diffusion studies, where in spite of numerous mass transport investigations the determination of the energies of defect formation and migration has not led to an unique conclusion.

Early in the past, there have been efforts to clarify this situation by showing how slight stoichiometry deviations can account for the range of observed creep activation energies. Cummerow [1] analysed firstly the possible rate limiting processes for diffusional creep as intrinsic/extrinsic lattice vacancy mechanisms; he arrived at a qualitative explanation for the variety of activation energies noted in its creep data. A more formal approach of the creep energy variation with stoichiometry was preliminary investigated by Hurm and Escaig [2]. Our more rigorous treatment based on the same approach confirms their general conclusions about possible mass transport mechanisms, dependent upon nature and concentration of impurities, but it brings out some important precisions including a partial re-interpretation of the Hurm and Escaig results.

The present paper is aimed at combining a

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detailed study of temperature and point defect concentration dependence of the creep activation energy in MgO, with the necessary appraisal of self-diffusion results used for numerical applications. Both cases of an excess of anion vacancies (such in Li^+-, K^+-, Na^+-doped MgO) and cation vacancies (such in Al^{3+}, Fe^{3+}-doped MgO) will be considered in the next section.

2. Apparent activation energy of mass transport in binary oxides

2.1. Case of anion vacancies in excess

Several studies on the diffusion-controlling creep of Li^+-doped MgO have been reported in the literature [2–5]. In terms of lattice diffusion by a vacancy mechanism, this corresponds to an excess of anion vacancies.

It has been shown for diffusion-controlled creep processes in ionic solids [6], the phenomenological vacancy diffusion coefficient is, in general, a complex diffusivity which is a combination of individual atomic mobilities for each charged species. This results from the coupling between various ion fluxes which is required in order to have no net electrical current flowing from sources to sinks in the crystal during creep.

For a vacancy mechanism, the Mg^{2+} and O^{2-} ion lattice diffusivities can be written $D_{\mathrm{Mg}} = [\mathrm{V_{Mg}}]D^0_{\mathrm{VMg}}$ and $D_{\mathrm{O}} = [\mathrm{V_O}]D^0_{\mathrm{VO}}$, where D^0_{VMg} and D^0_{VO} are the cation and anion intrinsic vacancy diffusion coefficients and $[\mathrm{V_{Mg}}]$ and $[\mathrm{V_O}]$ are the cation and anion vacancy concentrations, respectively. For pure or moderately doped MgO the ionic ratio $D_{\mathrm{O}}/D_{\mathrm{Mg}}$ controls the value of the phenomenological diffusion coefficient which can be written:

$$D_{\mathrm{mol}} = \frac{D_{\mathrm{O}}}{1 + \dfrac{D_{\mathrm{O}}}{D_{\mathrm{Mg}}}}. \tag{1}$$

Let us consider a Li^+-doped MgO crystal, the impurity content of which is specified by the substitutional atomic concentration of the monovalent cation $x = [\mathrm{Li_{Mg}}]$. The charge neutrality condition gives:

$$[\mathrm{V_{Mg}}] = [\mathrm{V_O}] - \frac{x}{2} \tag{2}$$

and the Schottky equilibrium writes:

$$[\mathrm{V_O}]\,[\mathrm{V_{Mg}}] = K_{\mathrm{S}} = \exp - (H_{\mathrm{FS}}/kT) \tag{3}$$

with H_{FS} is the energy needed to create a pair of isolated Mg- and O-vacancies. Solving for $[\mathrm{V_O}]$, one obtains the anion vacancy concentration:

$$[\mathrm{V_O}] = \frac{x}{4}\left[1 + \left(1 + \frac{16K_{\mathrm{S}}}{x^2}\right)^{1/2}\right]. \tag{4}$$

The ratio of the total to the intrinsic anion vacancy concentration thus can be written:

$$S = \frac{x}{4K_{\mathrm{S}}^{1/2}}\left[1 + \left(1 + \frac{16K_{\mathrm{S}}}{x^2}\right)^{1/2}\right] \geqslant 1. \tag{5}$$

The phenomenological diffusion coefficient is now a function of the temperature T and of the monovalent cation impurity concentration x, given by

$$D_{\mathrm{mol}} = \frac{S K_{\mathrm{S}}^{1/2} D^0_{\mathrm{VO}}}{1 + S^2 \dfrac{D^0_{\mathrm{VO}}}{D^0_{\mathrm{VMg}}}}. \tag{6}$$

One can now calculate the logarithmic derivative of the phenomenological diffusion coefficient with respect of $(kT)^{-1}$. This represents the self-diffusion activation energy in the limiting conditions of a true exponential variation of the diffusion coefficient; it means an apparent activation energy in transition regions, where of course, the variation is no more exponential, but where experimental curves on a semi-log plot would be locally close enough to straight lines, allowing for the determination of the apparent activation energies.

One found:

$$\Delta H_{\mathrm{D}}(T,x) = -\left[\frac{\partial \log D_{\mathrm{mol}}}{\partial\left(\dfrac{1}{kT}\right)}\right]_x = I + Q - \left(\frac{\Delta H_{\mathrm{m}} + 2Q}{1 + S^2 D}\right) \tag{7}$$

where $I = H^{\mathrm{Mg}}_{\mathrm{m}} + (H_{\mathrm{FS}}/2)$, with $H^{\mathrm{Mg}}_{\mathrm{m}}$ the migration enthalpy of magnesium

$$Q = \frac{H_{\mathrm{FS}}}{2}(1 + u)^{-1/2} \text{ with } u = \frac{16K_{\mathrm{S}}}{x^2}$$

$\Delta H_{\mathrm{m}} = H^{\mathrm{Mg}}_{\mathrm{m}} - H^0_{\mathrm{m}}$, with H^0_{m} the migration enthalpy of oxygen and

$$D = \frac{D^0_{\mathrm{VO}}}{D^0_{\mathrm{VMg}}} = \frac{D^0_{\mathrm{O}} \exp \dfrac{-H^0_{\mathrm{m}}}{kT}}{D^0_{\mathrm{Mg}} \exp \dfrac{-H^{\mathrm{Mg}}_{\mathrm{m}}}{kT}}.$$

In order to discuss the possible existence of various rate limiting diffusional processes for creep depending on temperature, it is convenient to write down the derivative of $\Delta H_{\mathrm{D}}(T, x)$ with respect to $(kT)^{-1}$, from Equation 7. This turns out to be relatively simple and reads:

$$\left(\frac{\partial\, \Delta H_{\mathrm{D}}}{\partial(1/kT)}\right)_x = \frac{H_{\mathrm{FS}}^2\, u(1+u)^{-3/2}}{4(1+y)^2}\,(y^2 + by - 1) \tag{8a}$$

where $y(x, T) = S^2 D$ is always physically positive, and

$$b = 4\left[\frac{\Delta H_{\mathrm{m}}}{H_{\mathrm{FS}}} + (1+u)^{-1/2}\right]^2 u^{-1}(1+u)^{3/2}.$$

Therefore, Equation 8 can be rewritten as:

$$\left(\frac{\partial\, \Delta H_{\mathrm{D}}}{\partial(1/kT)}\right)_x = A\{y + 0.5\,[b - (b^2+4)^{1/2}]\} \tag{8}$$

where A is always a positive quantity and different from zero. It shows clearly, in the case for an excess of anion vacancies, the activation energy ΔH_{D} exhibits a minimum value only when the physical conditions (T, x) make the function $y = S^2 D$ depressed down to a value sufficiently smaller than unity.

2.2. Case of cation vacancies in excess

This case occurs generally by producing polycrystalline MgO without the use of additives such as LiF or by doping the crystal with a trivalent cation impurity. This has been done reasonably well with documented creep measurements in MgO [2, 7–11].

For moderately trivalent cation doped MgO, the phenomenological diffusion coefficient becomes:

$$D'_{\mathrm{mol}} = \frac{D_{\mathrm{Mg}}}{1 + \dfrac{D_{\mathrm{Mg}}}{D_{\mathrm{O}}}}\,. \tag{9}$$

Following the same lines as for an excess of anion vacancies, but solving now for $[\mathrm{V_{Mg}}]$ one obtains:

$$[\mathrm{V_{Mg}}] = \frac{x'}{4}\left[1 + \left(1 + \frac{16K_{\mathrm{S}}}{x'^2}\right)^{1/2}\right] \tag{10}$$

where the atomic trivalent cation concentration is denoted x' in the cation vacancy concentration.

The total ratio to the intrinsic vacancy concentration now becomes:

$$S' = \frac{x'}{4K_{\mathrm{S}}^{1/2}}\left[1 + \left(1 + \frac{16K_{\mathrm{S}}}{x'^2}\right)^{1/2}\right] \geqslant 1. \tag{11}$$

With these notations the phenomenological diffusion coefficient can be expressed in the following form

$$D'_{\mathrm{mol}}(T, x') = \frac{S'\, K_{\mathrm{S}}^{1/2}\, D^0_{\mathrm{VMg}}}{1 + S'^2\, \dfrac{D^0_{\mathrm{VMg}}}{D^0_{\mathrm{VO}}}}\,. \tag{12}$$

Taking again the logarithmic derivative of this diffusion coefficient one computes the activation energy

$$\Delta H'_{\mathrm{D}}(T, x') = I' + Q' - \left(\frac{\Delta H'_{\mathrm{m}} + 2Q'}{1 + S'^2 D'}\right) \tag{13}$$

with:

$$I' = I - \Delta H_{\mathrm{m}}$$

$$Q' = \frac{H_{\mathrm{FS}}}{2}(1+u')^{-1/2} \text{ with } u' = \frac{16K_{\mathrm{S}}}{x'^2}$$

$$\Delta H'_{\mathrm{m}} = -\Delta H_{\mathrm{m}}$$

$$D' = D^{-1}.$$

The derivative of $\Delta H'_{\mathrm{D}}(T, x')$ with respect to $(kT)^{-1}$ is given by the equation transposed from Equation 8 by changing u into u', y into y' and b into b' such that

$$y'(x', T) = S'^2 D';\ b' = 4\left[\frac{\Delta H'_{\mathrm{m}}}{H_{\mathrm{FS}}} + (1+u')^{-1/2}\right]^2 u'^{-1}(1+u')^{3/2}$$

so that again

$$\left(\frac{\partial\, \Delta H'_{\mathrm{D}}}{\partial(1/kT)}\right)_{x'} = A'[y' + 0.5(b' - (b'^2 + 4)^{1/2})] \tag{14}$$

where A' is always a positive quantity and different from zero.

Equation 14 now shows in the case for an excess of cation vacancies the activation energy for creep does not exhibit any minimum value as long as the function $S'^2 D'$ cannot be depressed down to a value smaller than unity.

3. Discussion on rate limiting processes for lattice diffusion controlled creep of MgO

The previous analysis shows that the intrinsic ion mobility ratio $D = (D')^{-1}$ controls the value of

D_{mol}. Given a D value, for example small enough as compared to unity (i.e. oxygen ions are by far the slowest moving species), then a minimum activation energy appears at some temperatures in the case for an oxygen vacancy excess (e.g. for Li^+-doped MgO); but correlatively, in the case for a magnesium vacancy excess (e.g. for Fe^{3+}-doped MgO), such a minimum should not be observed. Of course, the reverse would ensue should D be larger than unity.

In order to account for the observed variation of creep energies with temperature and composition quoted in the literature, using Equations 7 and 13, it is necessary to rely on precise self-diffusion data.

Unfortunately, in the case of MgO, self-diffusion measurements have not led to consistent interpretations of the data. Lindner and Parfitt [12], Harding and Price [13] and Wuensch *et al.* [14] measured the self-diffusion coefficient of Mg^{2+} ions, while Oishi and Kingery [15], Hashimoto *et al.* [16] and Shirasaki and Hama [17] did measurements of the self-diffusion of O^{2-} ions. Although it is difficult to identify any given set of self-diffusion data as representing either intrinsic or extrinsic behaviour and to deduce characteristic energies for defect formation and migration, one can, however, estimate from these previous works a reasonable value for the intrinsic mobility ratio D'. From part of the data of Harding [13] and Shirasaka and Hama [17], regarding them as intrinsic ones, the ratio D' can be estimated to vary from about 2×10^5 to approximately 2×10^3 in the temperature range 1100 to 2500° C within which most of the creep experiments have been performed (Table I).

TABLE I Activation parameters for diffusion in MgO. D' values deduced from extrapolated Arhhenius plots for Mg^{2+} and O^{2-} diffusion in [13] and [17]

T (° C)	$10^{-4}\,D'$	T (° C)	$10^{-3}\,D'$
1157	21	1727	10
1208	13.8	1832	7.5
1265	9.4	1949	5.71
1327	6.3	2080	4.47
1394	4.38	2227	3.27
1466	3	2394	2.5
1545	2.1	2584	1.88
1632	1.44		

Schottky defect formation: $H_{\mathrm{FS}} = 3.8$ eV [13, 17]
Magnesium migration: $H_{\mathrm{m}}^{\mathrm{Mg}} = 1.6$ eV [13]
Oxygen migration: $H_{\mathrm{m}}^{\mathrm{O}} = 2.7$ eV [15–17]

Thus it is clear that in the case for a cation vacancy excess, the apparent creep energy can never exhibit any minimum, while in the case for a moderate anion vacancy excess a minimum energy should be observed. A wide variety of creep energies is reported in the MgO literature. Among these, two groups of data show up: those from monovalent and those from trivalent cation doped crystals. In the first group [2–5] activation energies range from about 2.2 to 3.3 eV, while in the second one, they are about 5 eV [2, 7, 11]. From Equations 7 and 13, it can be shown that as large as Schottky enthalpy value as about 7.7 eV, the theoretical estimated value [18, 19], cannot account for as low an activation energy as observed in the extrinsic regime. Instead, creep data tend to support the view of Harding and Price [13] who claim to have located extrinsic and intrinsic diffusion regions of Mg^{2+} ions in MgO. As a result the migration enthalpy of Mg^{2+} ions is found to be about 1.6 eV and the formation enthalpy of a Schottky defect is deduced to be 3.8 eV.

Going on, we can now plot the variation of ΔH_{D} with temperature for different atomic concentrations of monovalent and trivalent cation impurities. The characteristic enthalpies for the defect formation and migration of the two species which have been used to draw the curves in Fig. 1 are reported in Table I.

The curves can help decide the rate controlling process for creep. They confirm and delimit the four processes expected from the analysis of Cummerow [1] and Hurm and Escaig [2].

In the case of intrinsic conditions (very high purity, or very high temperature) the intrinsic diffusion of oxygen, the slower moving ion, is always rate limiting with an activation energy $(1/2)H_{\mathrm{FS}} + H_{\mathrm{m}}^{\mathrm{O}} \simeq 4.6$ eV.

For extrinsic conditions with an excess of anion vacancies, the extrinsic diffusion of oxygen should become rate limiting at intermediate temperatures (depending on the impurity content x) with a minimum plateau energy of $H_{\mathrm{m}}^{\mathrm{O}} \simeq 2.7$ eV; at the lowest end of the temperature range, due to the deficiency of cation vacancies, extrinsic diffusion of magnesium should prevail with an activation energy of $H_{\mathrm{FS}} + H_{\mathrm{m}}^{\mathrm{Mg}} \simeq 5.4$ eV.

Finally, the third extrinsic process may be found in the case of cation vacancy excess. Under these conditions, due to the need for the creation of anion vacancies, extrinsic diffusion of oxygen should dominate at lower temperatures with an

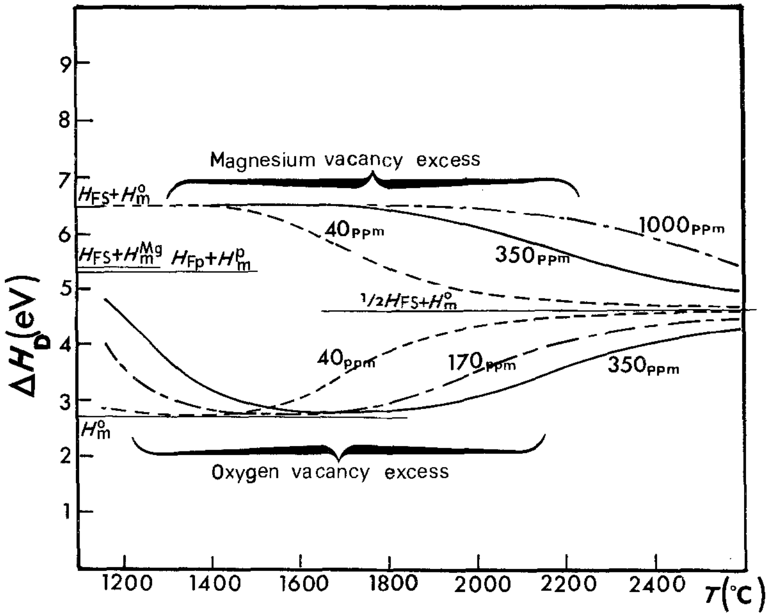

Figure 1 Variation of ΔH_D with temperature for different concentrations in at ppm of monovalent cation impurity case of oxygen vacancy excess and trivalent cation impurity case of magnesium vacancy excess.

activation energy, $H_{FS} + H_m^0 \simeq 6.5\,\text{eV}$, much higher than the intrinsic one.

Analysis of creep data obtained from polycrystalline MgO produced with an additive of 2 to 3 wt % LiF, where the Li^+ cation has been reported as the major impurity, suggests extrinsic oxygen diffusion as the rate limiting process in the temperature range 1200 to 1700° C. Creep studies in this material have been performed by Langdon and Pask [3], Bilde-Sorensen [4], Hurm and Escaig [2] and finally Dokks [5]. Activation energies were reported to be 2.2, 3.3, 2.6 and 2.4 eV corresponding to lithium contents 75, 300, 360 and about 40 at ppm, respectively. In order to improve the experimental data, a new quantitative chemical analysis of MgO samples used by Hurm and Escaig [2] has been resumed and is given in Table II.

Taking into account unavoidable experimental scatters both in the diffusion and in the creep measurements, the above observed energies may be viewed as being close enough to the well accepted value of 2.7 eV for extrinsic O^{2-} diffusion. However, in the study of Hurm and Escaig [2], the variation of creep energy with temperature, expected from Fig. 1, for their relatively high Li^+ content (360 ppm) was not observed; these authors concluded that for Li^+-doped MgO pipe diffusion rather than bulk diffusion might control the creep kinetics. Nevertheless, with regard to this disagreement, we would like to point out, from Fig. 1, that an average effective content of about 100 at ppm Li^+ impurities would easily account for a constant 2.7 eV energy over the whole temperature range 1200 to 1700° C. Whether the true values of the mobility ratio D' are larger than those used here, which would cause the minimum plateau in energy to extend over a larger temperature range, or the effective anion vacancy excess is lower than believed from the only cation charge balance, due to the presence of additional presumable anion impurities, is difficult to assess; at least it shows that the present discrepancy might not be so disturbing as previously thought.

The creep data reported for polycrystalline MgO doped with trivalent cation solutes (Al^{3+}, Fe^{3+}) are generally characterized by a relatively high activation energy, about 5.2 eV. Fig. 1 shows that this figure is clearly too low to represent the

TABLE II Impurity content of MgO polycrystals investigated in [2] (in at ppm)

	Si^{4+}	Al^{3+}	Fe^{3+}	Ca^{2+}	Na^+	K^+	Li^+	
Li^+ doped MgO	10	40	< 3	10	< 10	20	400	Effective monovalent cation content $\Sigma(M^+ - M^{3+} - 2M^{4+}) = 360$
Al^{3+} doped	200	1300	10	90	70	100	< 1	crept below 1500° C
MgO	110	1200	20	30	100	75	< 1	crept above 1500° C

extrinsic oxygen diffusion in this case, where activation energies below 1700° C are expected to be larger than at least 6 eV at any impurity content but the lowest ones (below 10 or 20 ppm only). Therefore, it may be of interest, as suggested by Hurm and Escaig [2], followed by Smyth [20], to consider a diffusion mechanism by neutral vacancy pairs. Since clearly, the formation energy of a neutral pair (i.e. an anion and a cation vacancy in first neighbour position) H_{FP}, is smaller than the Schottky energy H_{FS}, there exists a trend to favour the neutral vacancy pair over the isolated vacancy, extrinsic mechanism at lower temperatures. Albeit that H_{FP} and the pair migration energy $H_{\mathrm{m}}^{\mathrm{P}}$ are not known, a guess of the corresponding energy for mass transport is possible. Taking $H_{\mathrm{m}}^{\mathrm{P}} \simeq H_{\mathrm{m}}^{0}$ for the sake of simplicity and $H_{\mathrm{FP}} \simeq 0.66 H_{\mathrm{FS}}$ [18], one derives a value $\Delta H_{\mathrm{D}} = H_{\mathrm{FP}} \simeq 5.3$ eV, clearly below the range of extrinsic energies. Of course, although this value agrees quite well with the observed creep energies we cannot claim this mechanism is really evidenced in these experiments, due to the lack of precise independent determinations of the involved defect energies.

Hurm and Escaig [2] have reported that in Al^{3+}-doped specimens (see in Table II) there is a change below 1500° C in the creep energy which drops from 5.2 down to 2.6 eV. Electron microscopy reveals that below this temperature, aluminium impurities which are in the range 1000 at ppm in these crystals, are found merely precipitated into $\mathrm{MgAl_2O_4}$ spinel fine inclusions. Since recent analysis has shown the presence of monovalent cation impurities in their specimens in the range 100 to 200 at ppm (see in Table II), it seems reasonable to consider these Al^{3+}-doped samples below 1500° C as doped, in fact, by monovalent cations in concentration of the order 100 at ppm. The creep energy in this case is expected from Fig. 1 to be constant from 1200 to 1500° C and equal to 2.7 eV, just as it is observed. Therefore the observed transition below 1500° C in creep energy should be viewed as a transition toward O^{2-} extrinsic diffusion, rather than toward O^{2-} intrinsic pipe diffusion as previously suggested.

4. Conclusion

The variation of activation energy for mass transport by self diffusion of isolated vacancies has been established in a MO ionic crystal, depending upon the temperature, the nature and the number of composition vacancies. Because of anion–cation ambipolar coupling, three distinct regimes of extrinsic diffusion rate-controlled creep are in principle observable in MgO.

In the experimental temperature range and the monovalent cation impurity content investigated by several authors, a good correlation is found between observed creep energies and the transport energy by extrinsic diffusion of oxygen vacancies in excess. When MgO is doped with trivalent cations, in contrast, no such correlation is obtained. Instead, self diffusion by neutral vacancy pairs should prevail in the high temperature creep of these specimens.

The samples affected by Al^{3+} impurity precipitation in the study of Hurm and Escaig are not regarded to be as pure as previously presumed, but rather as slightly doped with monovalent cations. Accordingly, the transition observed in creep energy below 1500° C, from 5.2 down to 2.6 eV, has been re-interpreted like a change in the basic diffusion process, namely from a vacancy pair to an isolated vacancy mechanism when extra oxygen vacancies are introduced in the lattice as a result of Al^{3+} precipitation.

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