The Trouble with Activation Energies

Peter E. D. Morgan*

fresh from recent conference

“Interfaces in Functional Materials”

Irvine Fri 27th
etc

***Institute for
free-thinking,
retired, pensioned
-off scientists**

Abstract

The concept of “activation energy” (AE) is simple, but, it can only sensibly be applied to simple situations; – most solid state processes are complex.

For a simple unimolecular decomposition or change; for a simple bimolecular reaction etc., things are fairly straightforward.

Even when a molecule must change shape (as for enzymatic processes) to interact, and a series of sequential processes occur – in any particular temperature regime it is normally understood that the slowest process in that regime is rate determining and the associated activation energy may be measured.

On the other hand, when parallel processes occur, the situation changes and this will be seen to be quite common in solid state kinetic processes – as in the cases of sintering, with or without densification, grain-growth, creep and so forth.

Examples will be given from the literature of what the problem is, and how it can be tackled, so that unrealistically high AE (higher than any known diffusional processes) can be understood.

As for parallel processes, consider: – a molecule has two reversible tautomeric forms, a high temperature (HT) one, and a low temperature one (LT) and there is a temperature dependent equilibrium; only the HT one reacts in some way (say) with another molecule with a conventional activation energy.

Studying the kinetics, two temperature dependent processes will be occurring together:- the number of suitably structured HT molecules for reaction increases with temperature and the sub-set number sufficiently activated to react also increases in the usual way so the rate will rise as a product of the temperature dependence of the amount of the HT reacting tautomeric form (the effective concentration which might be exponential or otherwise) TIMES the temperature dependence of the rate reaction of the HT form. With usual log plot, measured $\mathbf{E_{total} = E_c + E_r}$

Whether such a model molecular situation exists, is unknown to me
– I solicit info. on this.

This parallel process situation is dealt with here to explain why “activation energies”, higher than for known diffusional processes, are frequently determined, ignored, bizarrely explained, or “hand-waved away”. Also where “activation energies” appear to change with temperature or may even be above the heat of vaporization/evaporation of the material: three somewhat tractable cases (many more difficult ones exist) have been chosen where “activation energies” are measured to be “anomalously high” (“oh really”! – “we didn’t notice!”):

(1) sintering, grain-growth, or creep of ceramic materials likely containing (but often not perceived) low level liquid, viz. above a eutectic/peritectic temperature in impure materials.

(2) Electrical conductivity resulting from mobile atoms or vacancies e.g. typified by zirconia/yttria.

(3) Creep, with no obvious liquid etc, but where “activation energies” appear to be high (epitomized by the Martin Harmer group’s defining/seminal creep work on very pure and carefully doped aluminas.)

Approximately, (maybe if exponential) then:

$$\mathbf{R = C \times \mathit{R} = C_0 e^{-Ec/RT}} \times \mathbf{\mathit{R}_0 e^{-Er/RT}}$$

R = reaction rate = concentration of reactants x rate of change

Where $\mathbf{C_0 e^{-Ec/RT}}$ = concentration of HT available to react at T

$\mathbf{\mathit{R}_0 e^{-Er/RT}}$ = rate of sufficiently activated subset reacting at T

Taking logs: $\mathbf{\log R = \log C_0 - E_c/RT + \log \mathit{R}_0 - E_r/RT}$

Plotting **logR vs 1/T :** $\mathbf{slope = - E_{total} = - (E_c + E_r)}$

Activation energies add up and give a high value.

Similar (often well disguised) situations occur in the solid state!

Example (1) – the presence of liquid in ceramics (and metals)

Should liquid phase be present in a ceramic (often undetected at low levels of ~0.01mol%, though enough to give complete grain-boundary coverage at 1μm grain-size) the mobility of species passing through the liquid, as for grain-growth certainly, and probably for sintering/densification and creep also, will be thermally activated in the usual Arrhenius mode.

In addition, the concentration of mobile species in the liquid will rise with temperature related to the heat of solution in the liquid etc. Moreover, this increasingly strong solution will lead to an increasing volume of liquid coverage as the temperature rises; this leads to complicated, 2,3 or more, parallel multiplied mechanisms reflected in the measured temperature dependence of the flux(s) of the process –this often then manifests itself as unphysically high "apparent activation energies" (higher even than the heat of evaporation/vaporization!); this is obviously unrealistic as a single, meaningful "activation energy" capable of being interpreted as suggesting any singular mechanism.

Electrical Conductivity Measurements to Detect Suspected Liquid Phase in the Al_2O_3-1 mol% TiO_2-0.5 mol% $NaO_{1/2}$ and Other Systen

PETER E. D. MORGAN* AND MICHAEL S. KOUTSOUTIS

J. Am. Ceram. Soc., 69 [10] C-254–C-255 (1986)

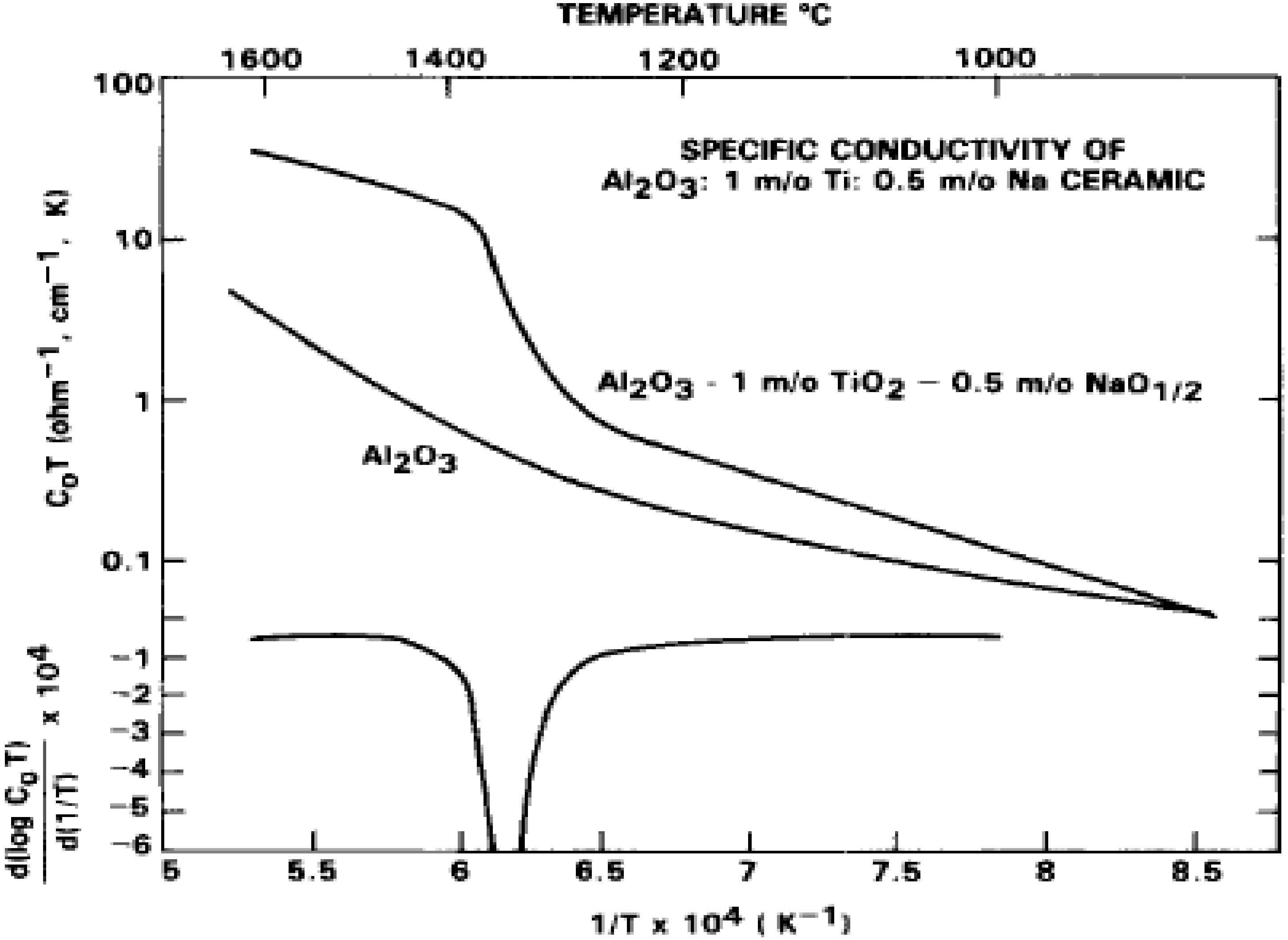


Fig.1. Specific conductivity (× temperature) vs reciprocal temperature for Al_2O_3-1 mol% TiO_2-0.5 mol% $NaO_{1/2}$ (lower curve is differential of upper one).

Liquid Phase and Electrical Conductivity in TiO_2 Added $BaTiO_3$ Ceramics

Shinichi MIURA, Ben HUYBRECHTS† and Masasuke TAKATA

Journal of the Ceramic Society of Japan 107 [5] 469-471 (1999)

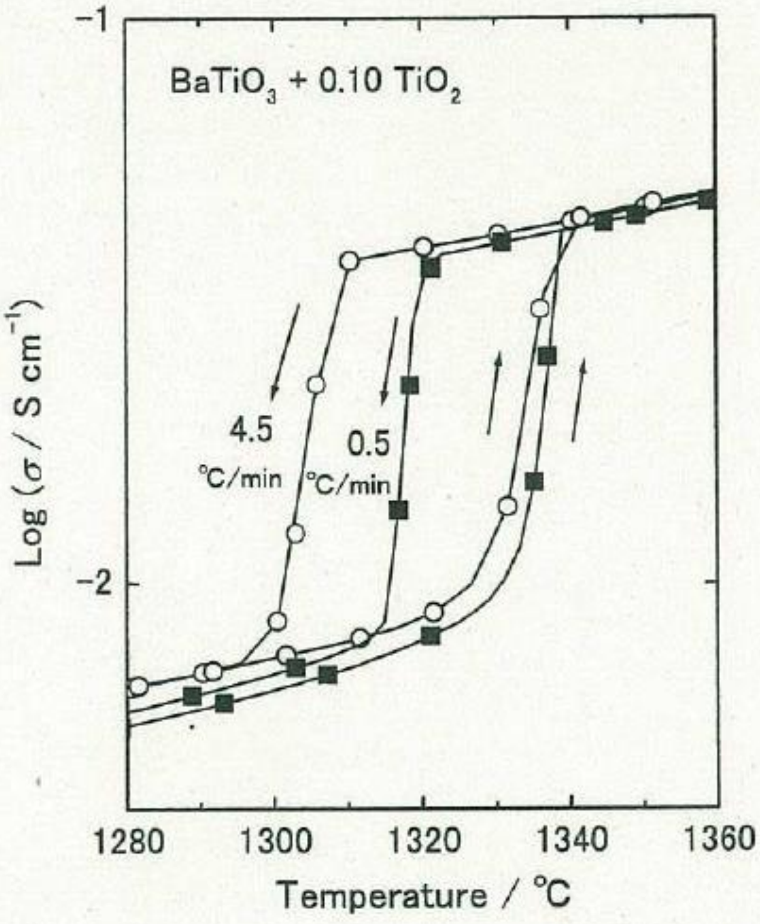
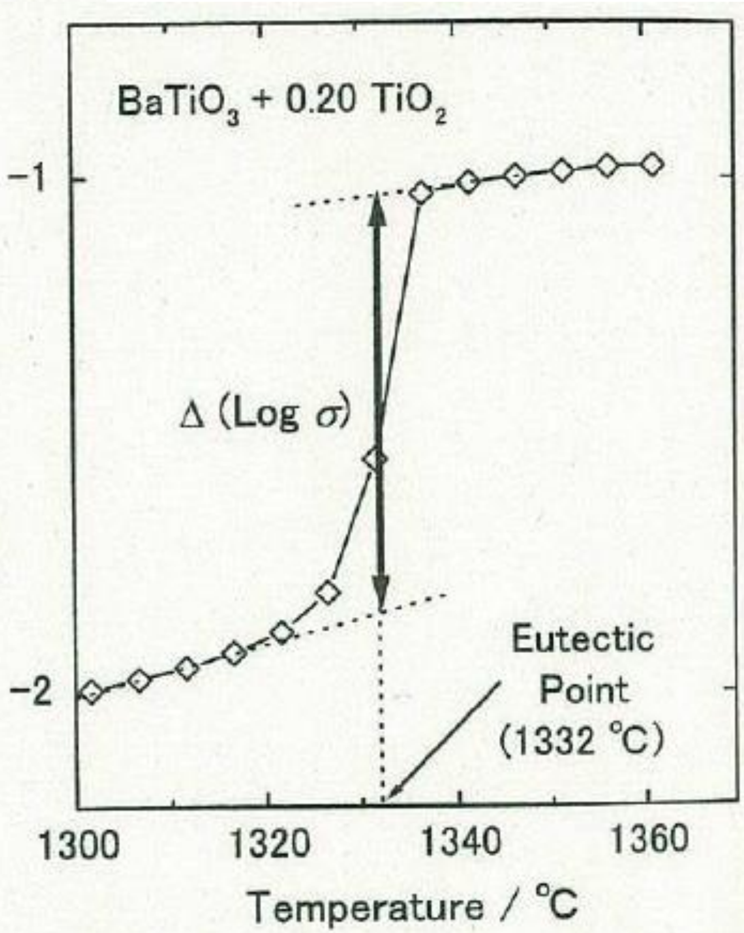


Fig. 2. Temperature dependence of electrical conductivity in $BaTiO_3+0.10$ TiO_2 polycrystalline samples around the eutectic point. The heating and cooling rate were 0.5 and 4.5°C/min.



In the temperature region 1250^{o}C-1350^{o}C, the slope (= “activation energy”) would seem to be very high (befitting, in this case, the growing amount of liquid **and** its higher conductivity) – should such liquid be unsuspected at low levels an incorrect conclusion might be achieved. The activation energy of conductivity in the pure liquid is certainly lower than in the solid. If grain-boundaries increasingly show any “liquid-like” behavior (or increased disorder or widening) as temperature rises, this would be manifested as a higher “activation energy” than expected for unchanging grain boundaries – this same effect would also appear in a radioactive tracer type diffusion measurement.

The fact that high “activation energies” are seen, in cases where GB diffusion is believed to be the operative mechanism, suggests that, indeed, grain boundaries are changing with temperature and this was prescient for indications now appearing using calculational methods.*

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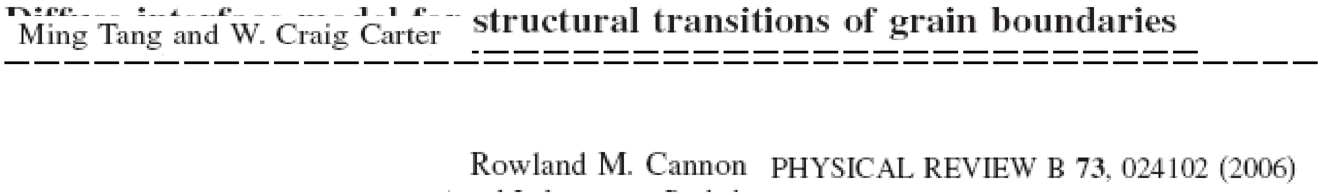
*e.g.



structural transitions of grain boundaries

Ming Tang and W. Craig Carter

Rowland M. Cannon

PHYSICAL REVIEW B 73, 024102 (2006)

Flow behaviour of aluminium-based materials at ultrahigh temperatures in the presence of a liquid phase

Lou BY, Huang JC, Wang TD, Langdon TG

MATERIALS TRANSACTIONS 43 (3): 501-509 MAR 2002

Experiments were conducted to determine the flow behavior of three materials at ultrahigh temperatures: an Al-6061 composite containing 20 vol% SiC whiskers and unreinforced Al-6061 and Al-1050 alloys prepared by casting. Tensile tests were performed at strain rates up to 5 x 10(-1) s(-1) and over a range of ultrahigh temperatures up to and above the temperatures where there is a small amou of liquidphase, High strain rate superplasticity was achieved in the composite material but not in the unreinforced alloys. For all three materials, it is shown that the true activation energy for flow changes from values of < 200 kJ mol(-1) at the lower temperatures. here there is no liquid phase to exceptionally high values in the presence of a liquid phase: these values are up to > 1000 kJ mol(-1) for the composite and the Al-1050 alloy. It is concluded that exceptionally high activation energies are an inherent feature of flow in materials containing a small amount of discontinuous liquid at temperatures immediately above the onset of partial melting.

ACTIVATION-ENERGIES FOR DENSIFICATION, CREEP, AND GRAIN-BOUNDARY SLIDING IN NITROGEN CERAMICS

RAJ R and MORGAN PED

JOURNAL OF THE AMERICAN CERAMIC SOCIETY
64 (10): C143-C145 1981

Abstract

The activation energies for densification, creep, and grain-boundary sliding in HP-Si_3N_4 *are consistent and large, approaching the heat of sublimation of* Si_3N_4*. If solution-precipitation through the intergranular glass (or fluid) is invoked as a common underlying mechanism, then it can be concluded that the high activation energy results from the high heat of solution of the crystal into the glass. This is consistent with the finding that it is difficult to retain* Si_3N_4 *in a glassy state.*

TRANSIENT CREEP-BEHAVIOR OF HOT ISOSTATICALLY PRESSED SILICON-NITRIDE

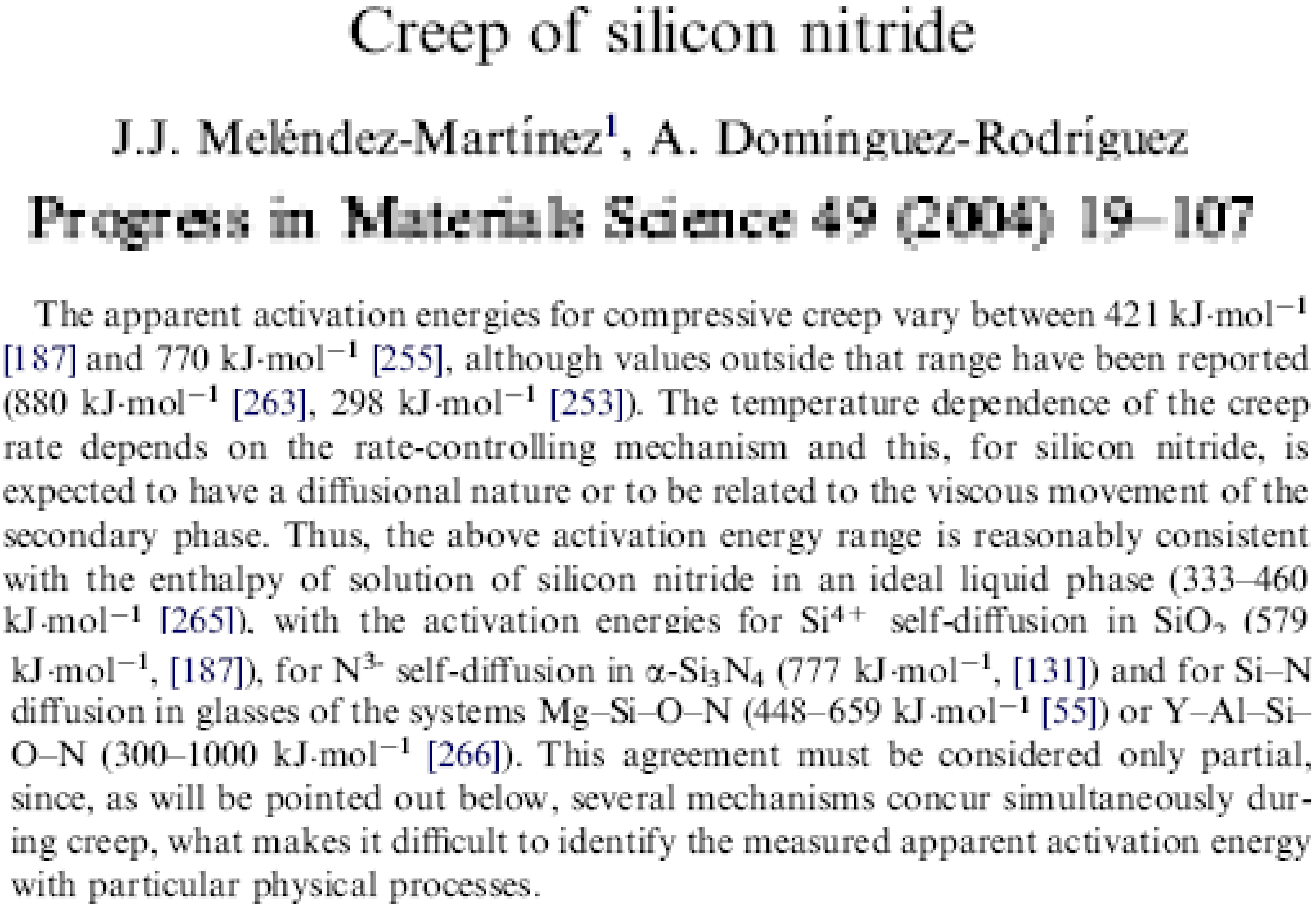
WIEDERHORN SM, HOCKEY BJ, CRANMER DC, YECKLEY R

JOURNAL OF MATERIALS SCIENCE 28 (2): 445-453 JAN 15 1993

From Abstract

It is suggested that the apparent activation energy for **creep** is determined by the mobility and concentration of diffusing species in the intergranular glassy phase.

Quoting Raj and Morgan



Creep of silicon nitride

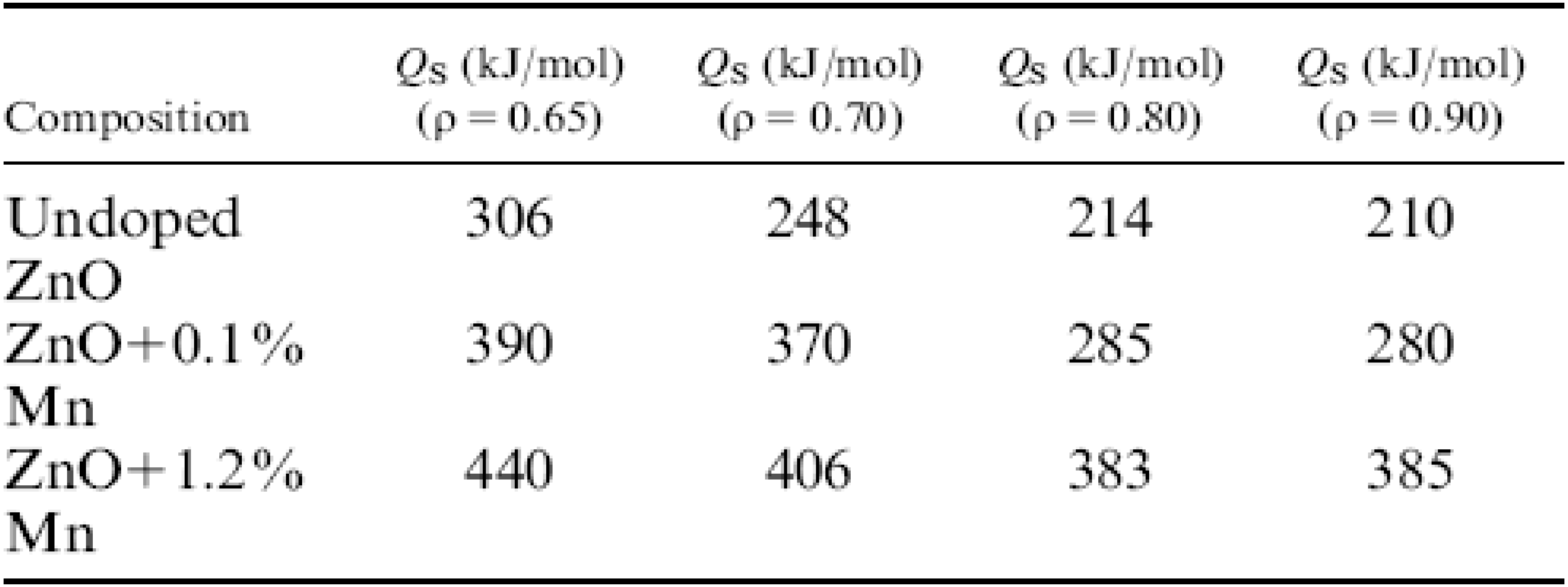
J.J. Meléndez-Martínez[1], A. Domínguez-Rodríguez

Progress in Materials Science 49 (2004) 19–107

The apparent activation energies for compressive creep vary between 421 kJ·mol^{-1} [187] and 770 kJ·mol^{-1} [255], although values outside that range have been reported (880 kJ·mol^{-1} [263], 298 kJ·mol^{-1} [253]). The temperature dependence of the creep rate depends on the rate-controlling mechanism and this, for silicon nitride, is expected to have a diffusional nature or to be related to the viscous movement of the secondary phase. Thus, the above activation energy range is reasonably consistent with the enthalpy of solution of silicon nitride in an ideal liquid phase (333–460 kJ·mol^{-1} [265]), with the activation energies for Si^{4+} self-diffusion in SiO$_2$ (579 kJ·mol^{-1}, [187]), for N^{3-} self-diffusion in α-Si$_3$N$_4$ (777 kJ·mol^{-1}, [131]) and for Si–N diffusion in glasses of the systems Mg–Si–O–N (448–659 kJ·mol^{-1} [55]) or Y–Al–Si–O–N (300–1000 kJ·mol^{-1} [266]). This agreement must be considered only partial, since, as will be pointed out below, several mechanisms concur simultaneously during creep, what makes it difficult to identify the measured apparent activation energy with particular physical processes.

Page 61 – 88 pages long review with 343 refs.

Table III. Sintering Activation Energies, Q_S, Determined at Several Densities, ρ, of Undoped and Mn-Doped ZnO in the Intermediate Stage



Composition	Q_S (kJ/mol) ($\rho = 0.65$)	Q_S (kJ/mol) ($\rho = 0.70$)	Q_S (kJ/mol) ($\rho = 0.80$)	Q_S (kJ/mol) ($\rho = 0.90$)
Undoped ZnO	306	248	214	210
ZnO+0.1% Mn	390	370	285	280
ZnO+1.2% Mn	440	406	383	385

Jiaping Han,[†,‡] P. Q. Mantas, and A. M. R. Senos

Sintering Kinetics of Undoped and Mn-Doped Zinc Oxide in the Intermediate Stage

J. Am. Ceram. Soc., **88** [7] 1773–1778 (2005)

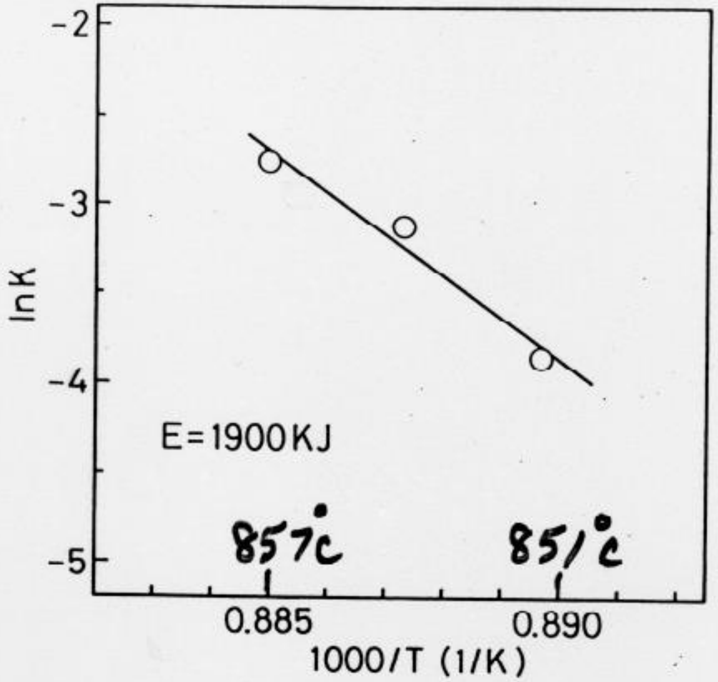


Fig. 12. Relation between ln *K* and $1/T$.

tained apparent activation energy in the present experiment includes the effect of the partial melting of the calcined powder surrounding the whiskers. Such a high activation energy is unexpected from a simple diffusion process. It seems more likely that the apparent activation energy for the phase conversion in the CAP method reflects not only the diffusion step but also the generation of the liquid phase needed for the initiation of the phase conversion (fig. 9) and the rearrangement at the interface between the 2212 and the 2223 phases with a bond departure process.

Example (2) – one simpler case that is becoming better understood

“Activation energies” are often seen to change with temperature leading to several “straight” line regions taken to indicate different mechanisms at different temperatures. This is all very specious* in complicated cases so here is probably just about the most simple case, now studied and argued over for more than fifty years.

The “two regions” of oxygen ionic conductivity in zirconia/yttria – about as simple as one could get, but which defied a plausible explanation until quite recently; being that the high temperature region is simply reflecting the temperature dependence of the mobility of the constant mobile vacancies, while the low temperature region is the summation of the activation energy of the mobility plus the activated concentration of mobile vacancies as released from Bevan type clusters or from the vacancy/zirconium pairs; and not from vacancy/yttrium pairs as once widely thought.

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*specious — **1.** Having the ring of truth or plausibility but actually fallacious: a specious argument. **2.** Deceptively attractive.

Effect of Aging on Yttria-Stabilized Zirconia

I. A Study of Its Electrochemical Properties

Junya Kondoh,[a] Tsuyoshi Kawashima,[b] Shiomi Kikuchi,[c] Yoichi Tomii,[d] and Yasuhiko Ito[e]

J. Electrochem. Soc., Vol. 145, No. 5, May 1998 1527

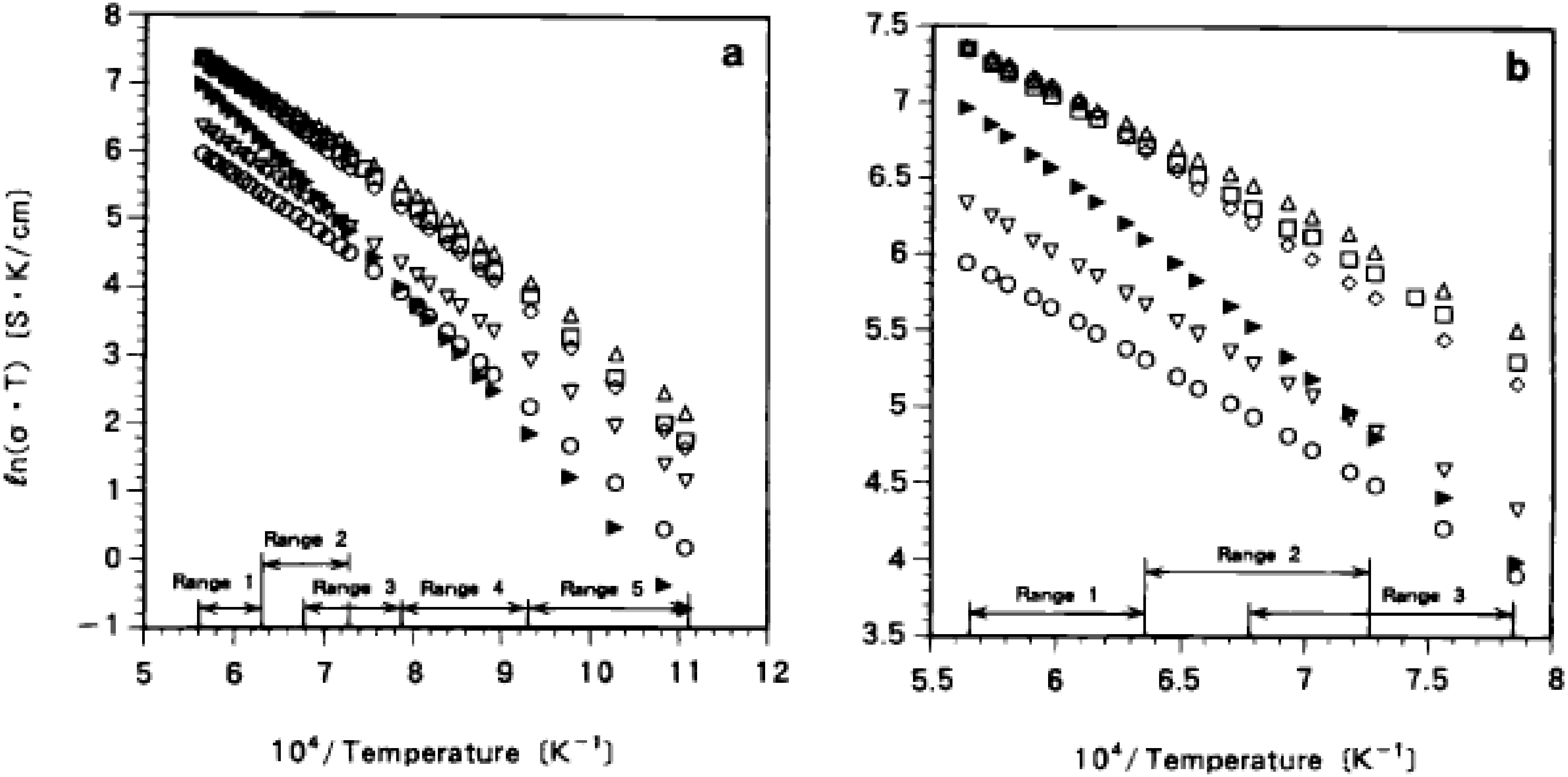


Fig. 4. Arrhenius plot of conductivity: (a) 1773 ~898 K, (b) 1773 ~1273 K; (○) 2YSZ, (▽) 3YSZ (Nikkato), (◇) 6YSZ, (△) 8YSZ (Nikkato), (□) 10YSZ, (▶) 15YSZ.

Electrical conductivity of the ZrO_2–Ln_2O_3 (Ln = lanthanides) system

Y. Arachi, H. Sakai, O. Yamamoto*, Y. Takeda, N. Imanishai

Solid State Ionics 121 (1999) 133–139

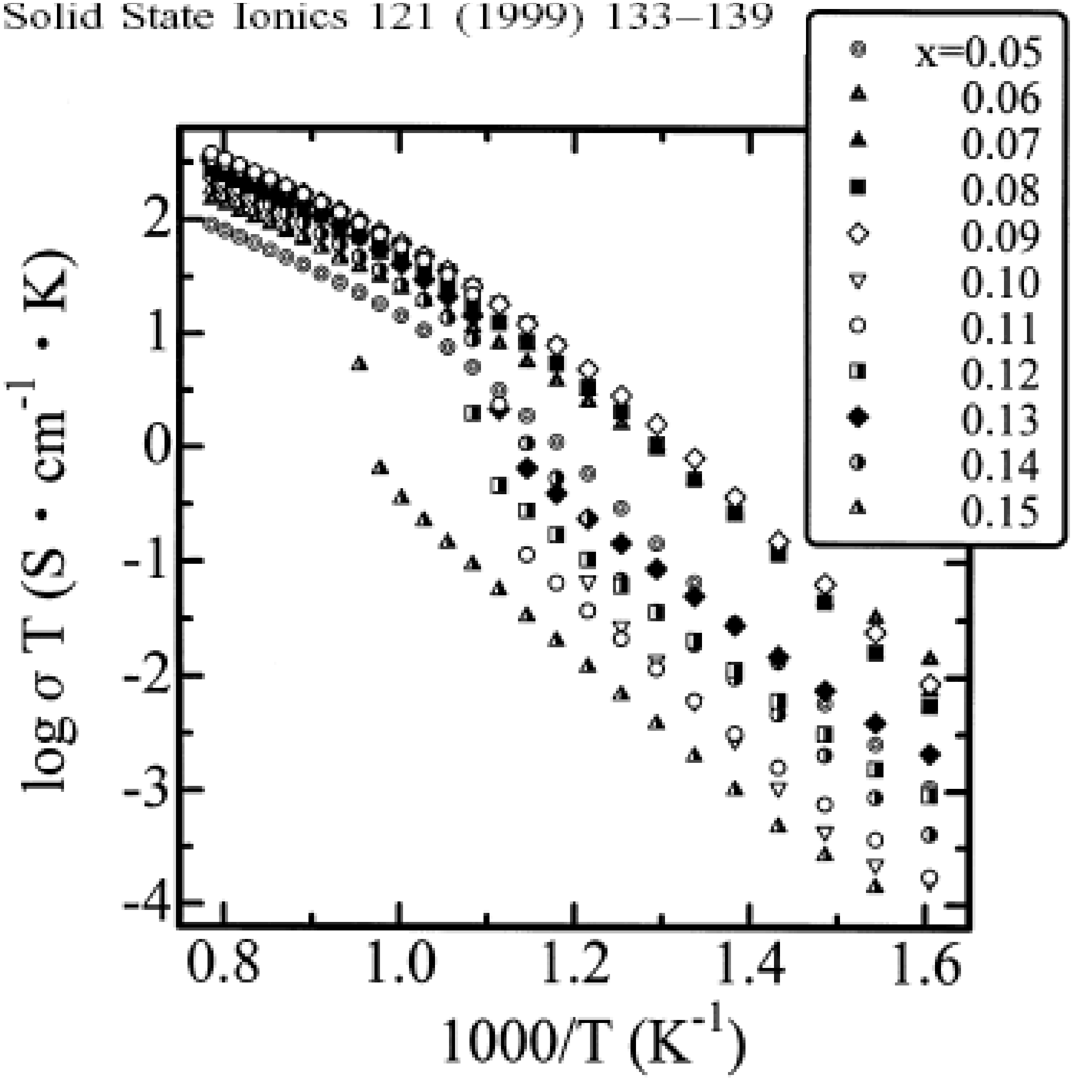


Fig. 3. Temperature dependence of the electrical conductivity for $(ZrO_2)_{1-x}(Sc_2O_3)_x$.

Study of the order–disorder transition in yttria-stabilised zirconia by neutron diffraction

Iain R. Gibson[a] **and John T. S. Irvine**[b]

J. Mater. Chem., 1996, **6**(5), 895–898

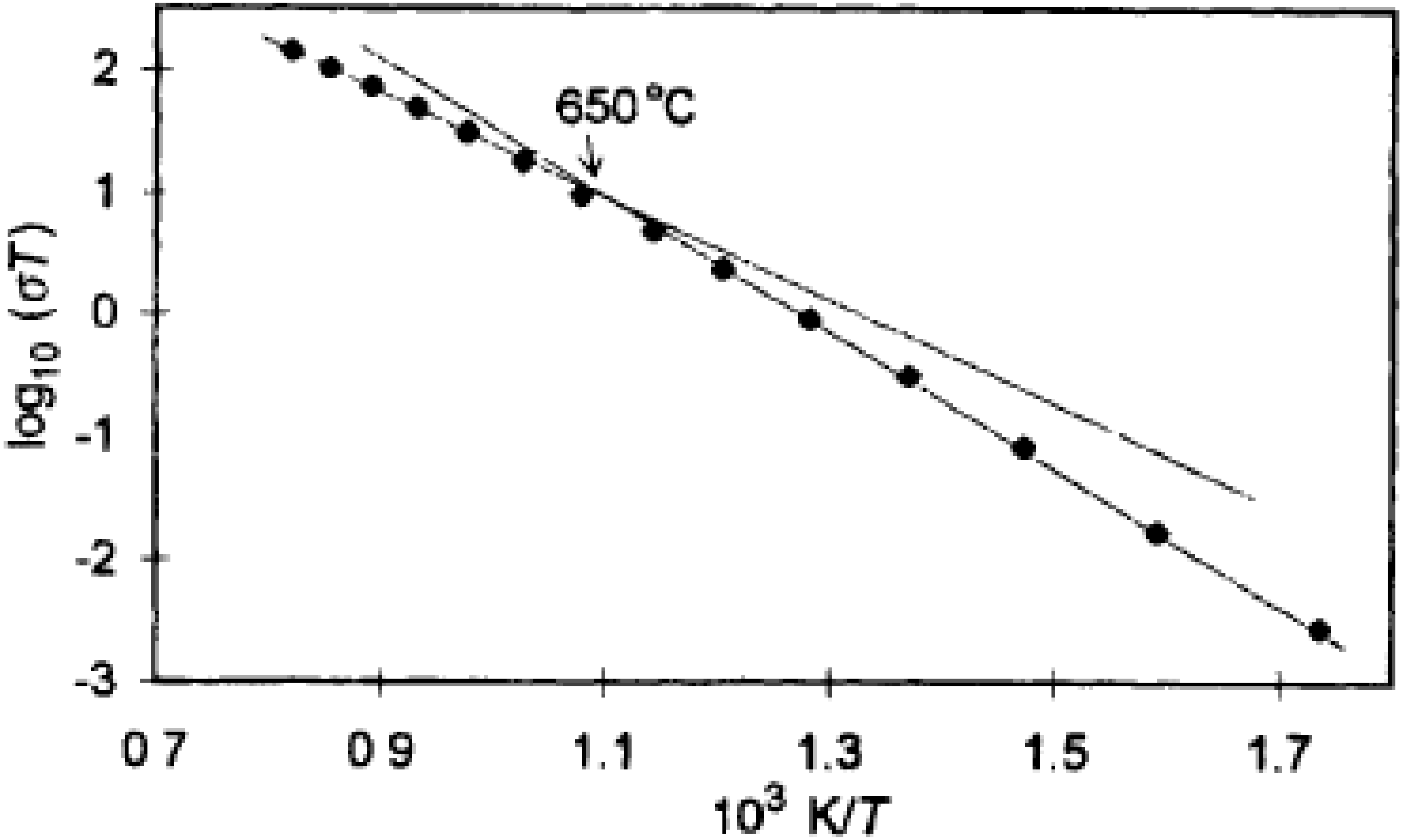


Fig. 1 Arrhenius conductivity plot for 8 mol% yttria-stabilised zirconia

Iain R. Gibson[a] and John T. S. Irvine[b]

J. Mater. Chem., 1996, 6(5), 895–898

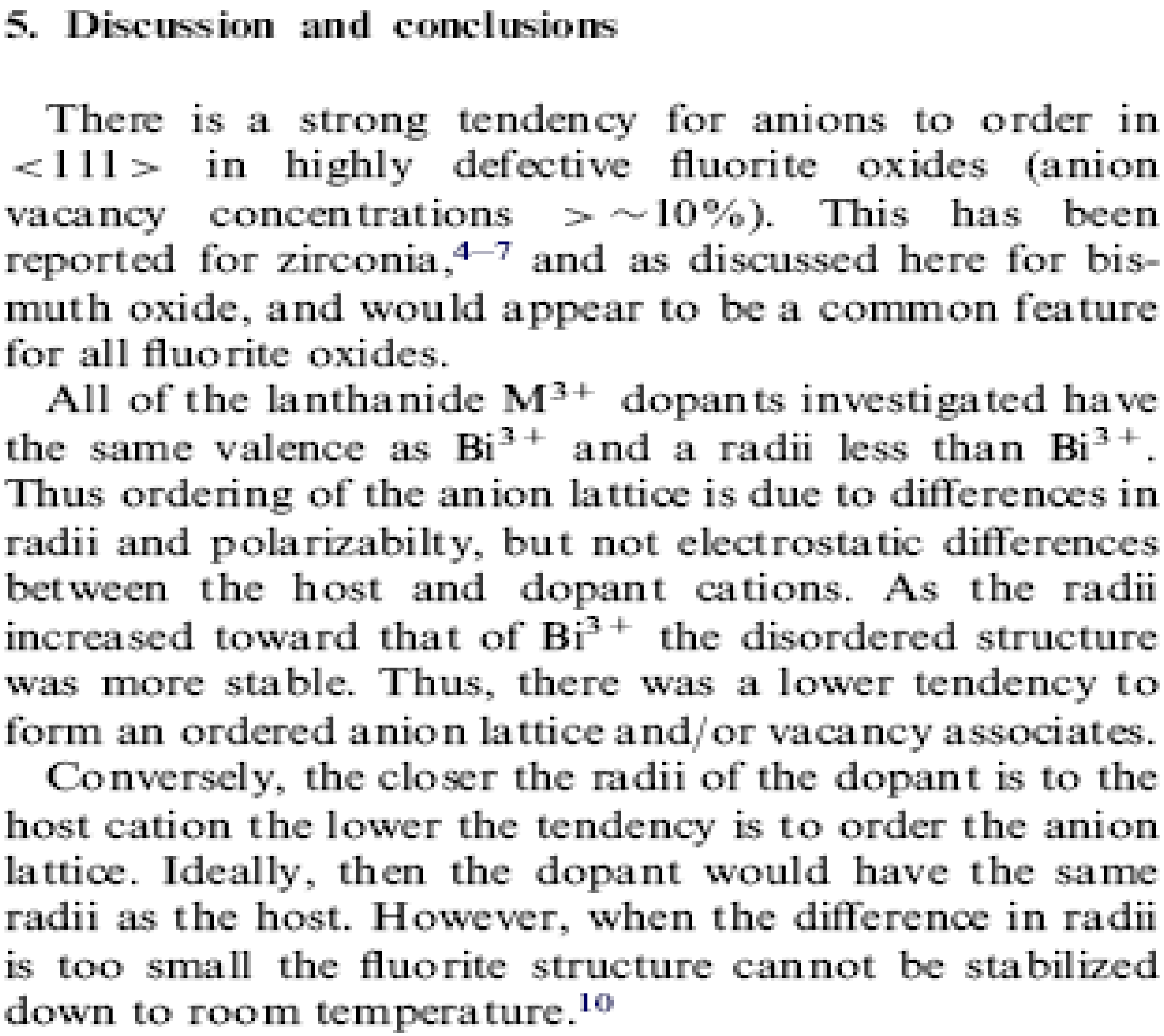
An increase in activation energy at low temperatures is in accord with the behaviour expected for some form of vacancy–dopant cation association. A number of such models for oxide-ion conduction have been developed to account for results from studies of ceria and perovskite systems.[5–7] Kilner and Steele[8] stated that the low-temperature activation energy comprised an oxygen vacancy migration enthalpy ($\Delta_m H$), and an association enthalpy ($\Delta_a H$), due to the vacancy–dopant complex. At higher temperatures, the vacancy–dopant complexes dissociate, allowing oxygen vacancies to migrate freely. The activation energy now contains only the migration enthalpy term, $\Delta_m H$.

J A Kilner and B C H Steele, in *Non-stoichiometric Oxides*, ed O T Sørensen, Academic Press, NY, 1981, pp 233–269

Effect of oxygen sublattice order on conductivity in highly defective fluorite oxides

Eric D. Wachsman*

Journal of the European Ceramic Society 24 (2004) 1281–1285



5. Discussion and conclusions

There is a strong tendency for anions to order in <111> in highly defective fluorite oxides (anion vacancy concentrations $> \sim 10\%$). This has been reported for zirconia,[4–7] and as discussed here for bismuth oxide, and would appear to be a common feature for all fluorite oxides.

All of the lanthanide M^{3+} dopants investigated have the same valence as Bi^{3+} and a radii less than Bi^{3+}. Thus ordering of the anion lattice is due to differences in radii and polarizabilty, but not electrostatic differences between the host and dopant cations. As the radii increased toward that of Bi^{3+} the disordered structure was more stable. Thus, there was a lower tendency to form an ordered anion lattice and/or vacancy associates.

Conversely, the closer the radii of the dopant is to the host cation the lower the tendency is to order the anion lattice. Ideally, then the dopant would have the same radii as the host. However, when the difference in radii is too small the fluorite structure cannot be stabilized down to room temperature.[10]

Electrical conductivity of the ZrO_2–Ln_2O_3 (Ln = lanthanides) system

Y. Arachi, H. Sakai, O. Yamamoto*, Y. Takeda, N. Imanishai

Solid State Ionics 121 (1999) 133–139

Manning et al. [17] suggested that $(Y'_{Zr}V_O)'$ is more likely to occur because of the expected random distribution of Y'_{Zr}. Kilner et al. [5] have shown that the effect of the binding enthalpy of an associate can significantly affect the population of free vacancies at low temperature. At lower temperatures association is almost complete, so that

$$[(Y_{Zr}V'_O)^{\cdot}] \gg [V_O^{\cdot\cdot}] \tag{4}$$

and

$$[V_O^{\cdot\cdot}] = A/T\exp(-E_a/RT) \tag{5}$$

where E_a is the association binding enthalpy, R the gas constant, T the absolute temperature, and A constant. The conductivity can be explained by Eq. (6)

$$\sigma = e\mu[V_O^{\cdot\cdot}] \tag{6}$$

where μ is the mobility, and e effective charge. The mobility μ is given by

$$\mu = B/T\exp(-E_m/RT) \tag{7}$$

where E_m is the enthalpy for motion and B the constant. The activation energy for conduction E_c is expressed as

$$E_c = E_a + E_m \tag{8}$$

At higher temperatures the complex of $(Y_{Zr}V_O)^{\cdot}$ dissociates completely to free $V_O^{\cdot\cdot}$ and Y'_{Zr}. The concentration of free $V_O^{\cdot\cdot}$ is independent on the temperature and equal to the total concentration of dopant Y^{3+}. Therefore, the migration enthalpy, E_m, could be estimated from the slope of the temperature dependence for conduction in the high temperature range. The association enthalpy could be calculated from the difference of the slopes in a lower temperature range and in a high temperature one.

Example (3) – creep without any obvious liquid phase– particularly as typified by the Martin Harmer group’s definitive and seminal work

Creep, even in the simplest case, involves diffusion and coupled grain-boundary sliding (we assume, as it will probably turn out, that bulk/lattice diffusion is, at best, a minor contributor, and that dislocation effects are minor in most ceramic cases (who knows monazite excepted!). The diffusion part can be rate limited by the rate of movement of the atoms in the boundary itself or limited by attachment or detachment from the boundary edges.

In the case of creep in doped aluminas, a set of Arrhenius lines is achieved as shown. The straight forward conclusion is that the larger doping cations “stuff” the larger interstices in the disordered grain-boundary attempting to achieve their preferred bond valence sums, which is why they go there). Also, in so doing, they occupy (and change/diminish) the mobile units that constitute the diffusion; the result is a great lowering of the rate of the energy and creep. The apparent greater activation energies for the inhibited cases is taken to be a greater activation energy for simple jumping but cannot really account for the fact that the diffusion values in the inhibited cases approaches the uninhibited values at the highest temperatures.

This becomes readily explicable if the measured “activation energy” is actually **$\sim E_c + E_m$** as detailed elsewhere. In this explanation the mobility is about the same when doped but the concentration of mobile species is greatly reduced. As the temperature rises the concentration of liberated mobile species activatedly increases (similar to the case of the Zr/Y oxide in example 2).

The concomitant events that “assist this liberation” of mobile units in the boundaries at higher temps are not yet known (as they are for example 2) but may include: 1) Some reversible diffusion of the dopes into the bulk away from the boundary; 2) an increasing disorder in the boundary – such as the diminishing of ledges and roughening of the edges; 3) an increase in the effective boundary width or 4) others!?

This emphasizes the importance of temperature quenching experiments, perhaps, to determine what may be occurring in such grain boundaries.

Densification and Grain Growth of Fe-Doped and Fe/Y Codoped Alumina: Effect of Fe Valency

M. D. Drahus, H. M. Chan,[†] J. M. Rickman, and M. P. Harmer

J. Am. Ceram. Soc., **88** [12] 3369–3373 (2005)

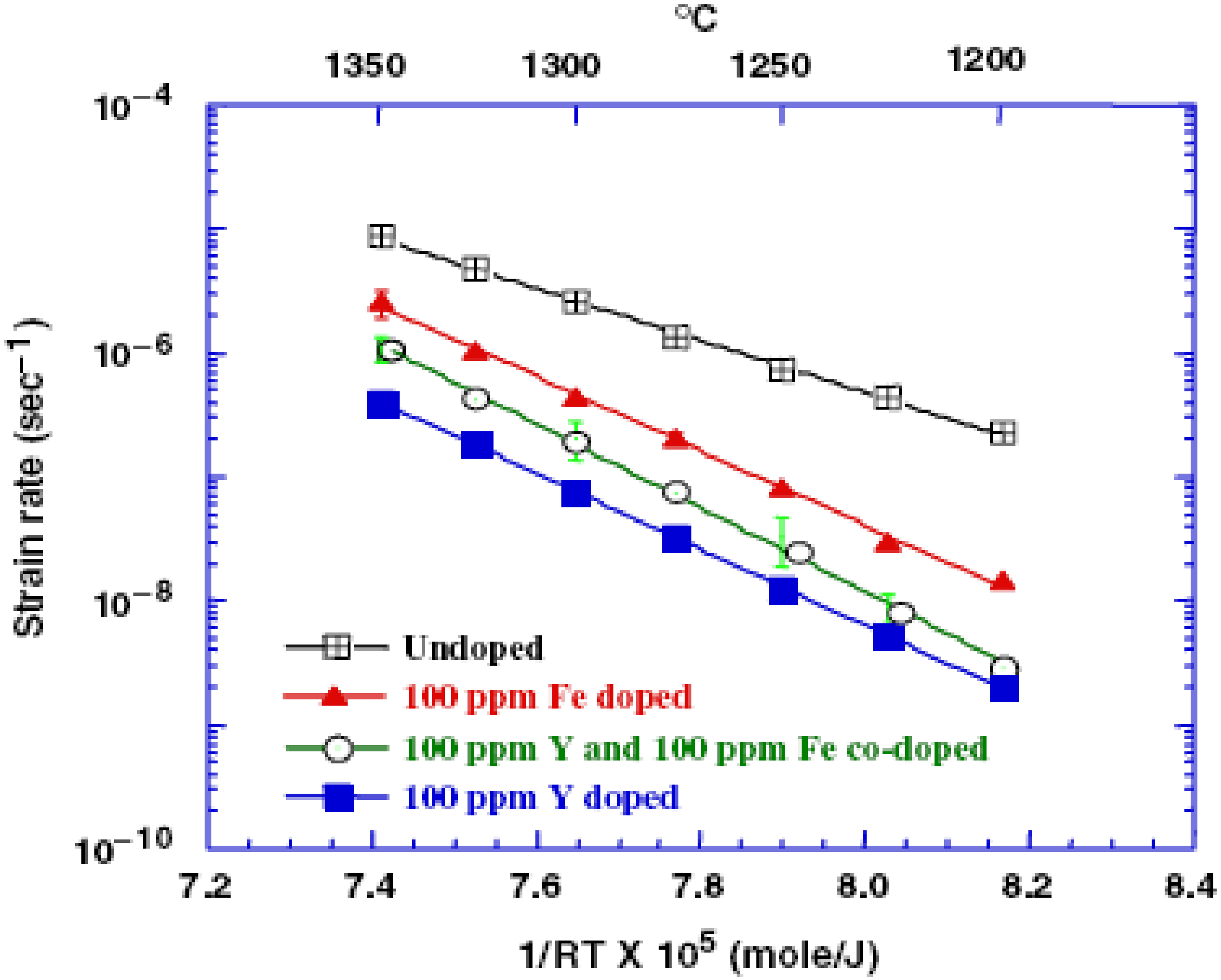


Fig. 1. Arrhenius plot of normalized creep rates for various alumina compositions. All the data were normalized to a grain size of 2.4 μm. Courtesy C. Wang.

ROLE OF SEGREGATING DOPANTS ON THE IMPROVED CREEP RESISTANCE OF ALUMINUM OXIDE

J. CHO, C. M. WANG, H. M. CHAN, J. M. RICKMAN and M. P. HARMER

Acta mater. Vol. 47, Nos 15, pp. 4197–4207, 1999

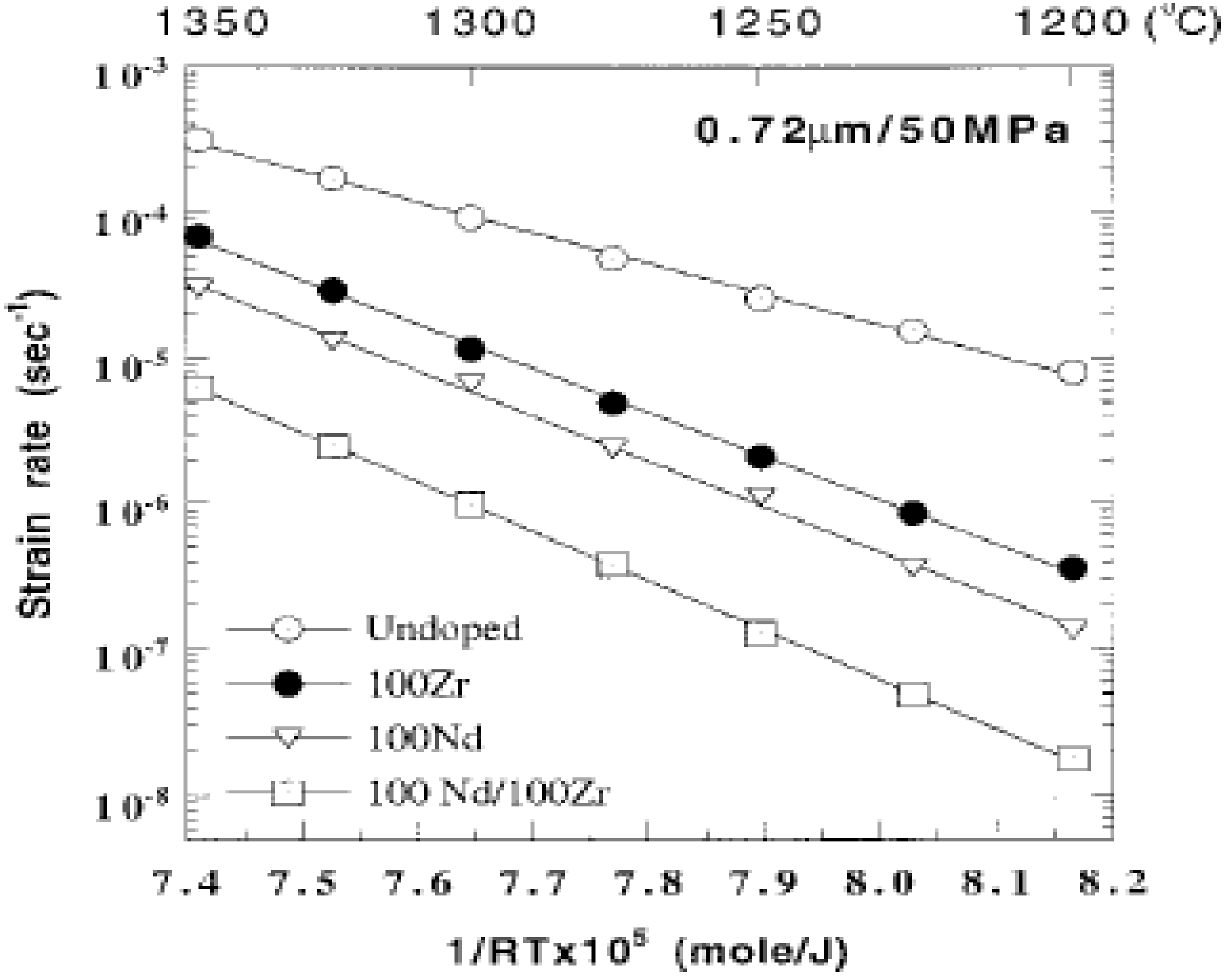


Fig. 2. Arrhenius plot of normalized steady-state creep rates for undoped, 100 p.p.m. Zr-doped, 100 p.p.m. Nd-doped, and 100/100 p.p.m. Nd/Zr-codoped alumina. The plots were normalized to a 0.72 μm grain size.

Conclusion

For a radioactive tracer diffusion experiment (say) on a single crystal, the concentration of mobile species (vacancies etc. in doped materials) changes little with temperature so that only the mobility temperature dependence is reflected in a measured activation energy for diffusion. Simple. You learned this in graduate school. Activation energy, always simple! Right? – Wrong!!

For many (most?) solid state processes e.g. sintering, densification, grain-growth, creep, and so forth. the concentration of mobile species likely changes with temperature as well – two at least, sometimes more, parallel processes occur simultaneously.

Flux = concentration of mobile species x mobility of mobile species

so that (approximately, maybe) : $\mathbf{E_{(apparent)} = E_{(concentration)} + E_{(mobility)}}$

For the three cases presented here, parallel processes are occurring for which the apparent temperature dependence of rates – “the apparent activation energies” – are summations of energies related to both concentration and mobility terms which are multiplied together to give an “apparent activation energy”.

This readily leads to values way above those of simple diffusional processes; only in a few publications, mentioned earlier, has this been discerned.

Conclusions drawn about simplified mechanisms, in myriad publications in many branches of materials science, from the measured, “apparent activation energies” will have to be re-evaluated (far from an easy task!).

In particular cases, higher **E** values have often been construed to suggest that bulk/lattice diffusion is operating when now, we suspect, from other techniques, that (e.g.) grain-boundary diffusion is much more likely to be the major contributor.