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Phonon scattering by oxygen vacancies in ceramics

Paul G. Klemens*

Department of Physics, University of Connecticut, Storrs, CT 06269-3046, USA

Abstract

The theory of phonon scattering by vacancies is applied to oxygen vacancies in zirconia and rutile. These vacancies are the major source of point defect scattering in stabilized zirconia. It is shown that the theory agrees well with thermal diffusivity reductions in reduced rutile. This lends confidence to the effect of oxygen vacancies on the thermal conductivity of stabilized zirconia, particularly in thermal barrier coatings. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Vacancies are strong phonon scatterers. They scatter in virtue of both missing mass and missing interatomic linkages. It has been shown that lattice distortion is not important, because it is strongest at the nearest linkages, which are missing. The resonance frequency of a vacancy is high, so that the scattering enhancement near the resonance frequency is not too significant. It is thus possible to ascribe scattering to the mass of the missing atom and to the missing potential energy of two atoms [1]. This theory agrees with thermal conductivity data of alkali halides, tin telluride and zirconium carbide. Stabilized zirconia has a low thermal conductivity and is thus used for thermal barrier coatings. The low conductivity can be attributed to the

oxygen vacancies which accompany the stabilizing solutes. The thermal conductivity reduction due to vacancies and solutes has been calculated [2], but a number of uncertainties impede comparison of theory with observation: the intrinsic conductivity cannot be measured but had to be estimated. At high temperatures there is a significant but variable radiative component. At low temperatures there is a reduction due to grain boundaries and due to an interchange of oxygen atoms with vacancies.

It is thus of interest to test the theory of scattering by oxygen vacancies and of thermal conductivity reduction in the case of rutile where thermal diffusivity measurements exist [3]. The thermal diffusivity of stoichiometric rutile (α_i) has been compared to the diffusivity α of four non-stoichiometric specimens with vacancy concentrations ranging from 1.67×10^{-3} to 1.2×10^{-2} per oxygen atom. In Table 1 the ratio $(\alpha/\alpha_i)_{\text{obs}}$ is given as function of temperature from 200°C to 800°C. The theoretical values $(\alpha/\alpha_i)_{\text{th}}$ are obtained as follows.

*Corresponding author. Fax: +1-860-486-3346; e-mail: klemens@uconnvm.uconn.edu.

Table 1
Thermal diffusivity reductions for TiO_{2-x}

T (K)	(ω_0/ω_m)	$(\alpha/\alpha_i)_{\text{th}}$	$(\alpha/\alpha_i)_{\text{obs}}$
$x = 0.005$			
473	1.76	0.91	0.89
673	2.10	0.93	0.94
873	2.39	0.95	0.95
1,073	2.65	0.96	0.96
$x = 0.011$			
473	1.17	0.83	0.82
673	1.52	0.88	0.91
873	1.61	0.89	0.92
1,073	1.79	0.91	0.90
$x = 0.031$			
473	0.71	0.68	0.63
673	0.84	0.73	0.73
873	0.96	0.77	0.77
1,073	1.06	0.80	0.80
$x = 0.037$			
473	0.65	0.64	0.57
673	0.77	0.70	0.66
873	0.88	0.75	0.72
1,073	0.97	0.78	0.74

2. Theory

In the temperature range where the spectral specific heat $C(\omega) \propto \omega^2$ and independent of T , the intrinsic phonon mean free path $l_i \propto \omega^{-2} T^{-1}$. Point defects scatter phonons with attenuation length $l_p \propto \omega^4$. Defining a frequency ω_0 such that $l_p(\omega_0) = l_i(T, \omega_0)$, the thermal conductivity with point defects becomes [4]

$$\lambda_p/\lambda_i = (\omega_0/\omega_m) \arctan(\omega_m/\omega_0), \quad (1)$$

where λ_i is the intrinsic thermal conductivity and ω_m the Debye frequency of the acoustic branch. It is given by $\omega_m = \omega_D/N^{1/3}$ where ω_D is the “per atom” Debye frequency and N the number of atoms per molecule. The intrinsic mean free path $l_i(\omega, T)$ is given by

$$1/l_i(\omega, T) = 2\gamma^2(kT/\mu a^3)(\omega^2/v\omega_m), \quad (2)$$

where γ is a Grüneisen anharmonicity parameter, a^3 the volume per atom, v the transverse wave speed, μ the shear modulus.

The spectral specific heat is $C(\omega) = 9k\omega^2/Na^3\omega_m^3$ and the intrinsic thermal conductivity becomes [2]

$$\lambda_i = \frac{1}{3} \int_0^{\omega_m} C(\omega) v l(\omega) d\omega = (3/2\gamma^2)(\mu v^2/N\omega_m) T^{-1}. \quad (3)$$

For substitutional atoms of mass $M + \Delta M$ and concentration c (per atom), the mean free path $l_p(\omega)$ is given by

$$1/l_p = (a^3/4\pi v^4) \omega^4 c (\Delta M/M)^2. \quad (4)$$

Equating $l_p(\omega_0)$ to $l_i(\omega_0, T)$

$$(\omega_0/\omega_m)^2 = (4\gamma^2/\mu a^3) [c(\Delta M/M)^2]^{-1} \quad (5)$$

and this can be used to obtain the fractional reduction in thermal conductivity from Eq. (1), as done for zirconia [2]. When measured values of λ_i are available, as for TiO_2 [5], one can use Eq. (3) to fit those parameters in Eq. (2) which are not well known: μ/γ^2 and $v \propto \sqrt{\mu}$. The former is then used in Eq. (5).

3. Non-stoichiometric rutile

For vacancies, the effective value of $\Delta M/M$ is [1]

$$\Delta M/M = -M_a/M - 2, \quad (6)$$

where M is the average mass per atom, M_a is the mass of the missing atom, and the term -2 accounts for the potential energy of the missing linkages, or twice the potential energy per atom. For an oxygen vacancy in TiO_2 , $\Delta M/M = -2.60$.

Other parameters are $a^3 = 10.6 \times 10^{-30} \text{ m}^3$, $N = 3$, $\mu = 4.4 \times 10^{10} \text{ Pa}$, $v = 3.2 \times 10^3 \text{ m s}^{-1}$, $\omega_m = 4.0 \times 10^{13} \text{ s}^{-1}$. The choice of μ , and therefore of v , is consistent with the choice of $\gamma^2 = 2$, because this gives λ_i of Eq. (3) a value of $2.8 \times 10^3 / T \text{ W m}^{-1} \text{ K}^{-1}$, as recommended in Ref. [5]. Thus, from Eq. (5),

$$(\omega_0/\omega_m)^2 = 1.11 \times 10^{-5} T/c. \quad (7)$$

For TiO_{2-x} , the concentration per atom c is $c = x/3$.

It is reasonable that, at low concentrations, vacancies have a negligible influence on the specific heat, so that the fractional reduction in thermal

diffusivity (α/α_i) is the same as for the conductivity in Eq. (1). Table 1 gives calculated values of (ω_0/ω_m) and of the diffusivity ratio $(\alpha/\alpha_i)_{th}$. These may be compared with the measured reductions $(\alpha/\alpha_i)_{obs}$.

There is good agreement between theory and observations, particularly at low vacancy concentration and high temperature, where vacancies are most likely to be uncorrelated. The close agreement is perhaps fortuitous, considering the simplifications in the theory. Nevertheless, this confirms the validity of the theory. For the largest values of x , there seems to be some reinforcement of scattering, if one wants to take the theory that seriously.

4. Implications for ZrO_2

Since vacancies are the strongest source of point defect scattering of phonons in stabilized zirconia, and in the technically important case of Y_2O_3 solutes the only significant source, one can now have confidence in the calculated lattice thermal conductivity. The weak temperature dependence frequently observed at high temperatures can be

attributed to a radiative component, which is controlled by residual porosity in sintered specimens, and also by cracks and splat boundaries in coatings. Around 1000–1200°C the lattice and radiative components are usually comparable.

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