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Thermal properties of a Bi_2O_3:Y_2O_3 oxygen conductor at low temperatures

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Specific-heat and thermal-conductivity measurements (1.7—40 K) are reported for the first time on a Bi_2O_3:Y_2O_3 oxygen conductor having a stabilized, defect-fluorite structure. Glasslike behavior is found in the properties measured, and the magnitudes of the coefficients involved are very similar to those found in amorphous materials. The thermal conductivity has a plateau region ~20—30 K and a T^2 temperature dependence below ~3 K. The specific heat has a maximum in C/T^3 at 12 K describable by a single Einstein term ($\omega = 33.1\ \mathrm{cm}^{-1}$) and a linear tunneling term resolvable below 3.5 K. The fitted Debye temperature is 248.9 K (±0.4%). This oxygen conductor has a large concentration of oxygen vacancies at elevated temperatures, but the Einstein term indicates that the majority of these vacancies is ordered at low temperatures. Using the vacancy concentration from the Einstein term, we find excellent agreement with the theory of McWhan *et al.* for the coefficient of the tunneling term. Comparisons are made with the low-temperature properties of stabilized zirconias and the alkali-metal β-aluminas.

I. INTRODUCTION

Materials with large ionic conductivities have received considerable recent attention, both as a way of studying diffusion mechanisms in the presence of a large concentration of diffusing ions and also as potential materials for energy-storage, fuel-cell, and oxygen-sensor applications. In general, these ionic conductors are characterized by locally disordered structures, such as the conduction plane in the alkali-metal (M) β-aluminas or the oxygen vacancies in the stabilized zirconias, and measurements of the thermal and dielectric properties of these materials at low temperatures are a useful means of studying this disorder. The analogy here is with the low-temperature behavior of *glassy* materials which universally display a distinctly non-Debye signature, for example: (1) a large maximum in C/T^3 around 10 K describable by an Einstein term(s), where C is the specific heat, (2) a linear term in the specific heat below ~3 K, $C_t \propto T$, (3) a plateau in the thermal conductivity K at ~10 K, (4) a quadratic T dependence, $K \propto T^2$, below ~3 K, and (5) a frequency-dependent minimum in the dielectric constant at ~0.1 K at radio frequencies. With the exception of (1) above, these properties are generally explained by a two-level tunneling model with a (nearly) constant density of states,[1] the latter being postulated on an *ad hoc* basis due to the topological disorder in glasses.

The low-temperature, excess specific heats of the silver and alkali-metal β-aluminas have been attributed to Einstein terms,[2] and the Einstein frequencies correlated well with Raman frequencies in the 28—82 cm^{-1} range. These frequencies in the M β-aluminas are also evident in the microwave spectra.[3] At the lowest temperatures a linear specific-heat term was found[2] and interpreted as the cation-tunneling contribution. A quadratic T dependence of the thermal conductivity of several β-aluminas at low and ultralow temperatures has also been reported.[4]

Perhaps the most thoroughly measured ionic conductor has been the classic[5] oxygen conductor ZrO_2:Y_2O_3. Here the Y_2O_3 content not only stabilizes the fcc fluorite structure but also creates oxygen vacancies, and low-temperature dielectric and thermal measurements on an 8-wt.% Y_2O_3—stabilized zirconia have been reported from 0.03 to 50 K.[6–8] All five of the glasslike properties mentioned above have been observed in these measurements, and the magnitudes of the coefficients involved (e.g., $C_t \propto T$, $K \propto T^2$) are surprisingly close to the values found in amorphous materials. Moreover, techniques have recently been developed to stabilize *tetragonal* ZrO_2:Y_2O_3 at room temperature,[9] and low-temperature measurements[10] on this material (above 1 K) suggest that these glasslike properties are insensitive to whether the host zirconia lattice is cubic or tetragonal. A ubiquitous problem in studying these zirconias is the hafnia content which contributes a Schottky term in the specific heat at low temperatures due to the electric quadrupole moments of ^{177}Hf and ^{179}Hf.[6,10] This hafnia contribution, which can mask the tunneling term, is evident even in the hafnia-refined, nuclear grade ZrO_2:Y_2O_3.[7]

The bismuth sesquioxide, oxygen-conducting materials have gained considerable, recent attention.[11] These materials have oxygen conductivities up to ~10^2 larger than the stabilized zirconias at elevated temperatures, and Bi_2O_3 bears many similarities to ZrO_2. Namely, pure bismuth sesquioxide has a (defect) fluorite phase (δ phase) above 730 °C which undergoes a destructive phase transition to a monoclinic structure at lower temperatures. Several lanthanum-series oxides are effective in *stabilizing* the defect-fluorite structure at lower temperatures (e.g., Yb_2O_3, Er_2O_3, Y_2O_3, Dy_2O_3, Gd_2O_3). The purpose of this paper is to report the first low-temperature measurements on a bismuth sesquioxide, oxygen-conducting material, wherein the stabilizing oxide is Y_2O_3 (25 mole %). This defect-fluorite material contains a very large concentration of oxygen vacancies (see below), and the purpose of these measurements was to investigate what similarities exist with the zirconias and the M β-aluminas.

II. EXPERIMENTAL METHODS AND RESULTS

Ceramic samples of the Bi_2O_3:Y_2O_3 material were prepared by conventional methods. Powders of Bi_2O_3 (99.5%) and Y_2O_3 (99.9%) were mixed and calcined at 800 °C for 8 h, and final pellets were sintered at 950 °C for 1 h. The composition was 25 mole % Y_2O_3, which is approximately the minimum amount needed to stabilize the fluorite phase.[11] X-ray analyses on the ceramic samples confirmed the presence of a single-phase, fluorite structure (lattice constant, 5.494 Å). Four-terminal dc resistivity measurements were made up to 600 °C on one of the samples, and these resistivity data agree very well with published data[11]; for example, the resistivity at 500 °C is 77 Ω cm, compared with 2560 Ω cm for ZrO_2+8 wt. % Y_2O_3 at the same temperature.

The large Y_2O_3 content needed to stabilize the fluorite phase in Bi_2O_3:Y_2O_3 translates into a large concentration of oxygen vacancies. Relative to the MO_2 fluorite structure, this composition is

$$(Bi_{0.75}Y_{0.25})O_{1.5}V_{0.50}$$

compared to

$$(Zr_{0.913}Y_{0.087})O_{1.957}V_{0.043}$$

for the stabilized zirconia mentioned above, where V represents the oxygen vacancy.

The specific-heat sample was a ceramic pellet (3.829 g) fixtured with a heater (343 Ω) and a carbon-chip resistor thermometer (10 mg). The addenda constituted 1.2 wt. % and contributed 9–4 % of the total heat capacity in the range 1.7–40 K, respectively. The adiabatic calorimeter described previously[12] was used, and $\Delta T/T$ values were maintained less than 3%. The uncertainty in the method is believed to be less than ±5%. Above 20 K, however, the uncertainty in the absolute temperature is ~0.1 K; while this does not affect C (since ΔT's are involved), it does affect C/T^3 (see below).

The thermal conductivity sample was a 2.54-cm-long bar with an A/l ratio 0.0846. The two-thermometer, linear-heat-flow method was used in the same calorimeter,[13] and the uncertainty in the method is believed to be approximately less than ±5%.

The measured specific-heat data are shown in Fig. 1 where the data are plotted as C/T^3 to illustrate the non-Debye behavior. Two features are apparent: (1) There is a broad maximum in C/T^3 at about 12 K, and (2) C/T^3 increases rapidly with decreasing temperature below 4 K. These features have been seen in the M β-aluminas[2] and in stabilized zirconias,[6–8] and in the analyses below we will assume that the first feature is due to an Einstein term, the second feature to the tunneling motions associated with disordered oxygen vacancies.

The measured thermal conductivity data are shown in Fig. 2. These data display classic glasslike behavior: plateau region around 20 K, and a quadratic temperature dependence below 3 K. Moreover, the magnitude of the quantities are very similar to those found in glasses; that is, the plateau thermal conductivity is ~3 mW cm^{-1} K^{-1}, and below 3 K, $K \cong 1.2\times10^{-4}T^2$ W cm^{-1} K^{-1}. For comparison, in ZrO_2:Y_2O_3 the plateau thermal conductivity is ~10 mW cm^{-1} K^{-1}, and in the quadratic region, $K \sim 8\times10^{-5}T^2$ W cm^{-1} K^{-1}.[8]

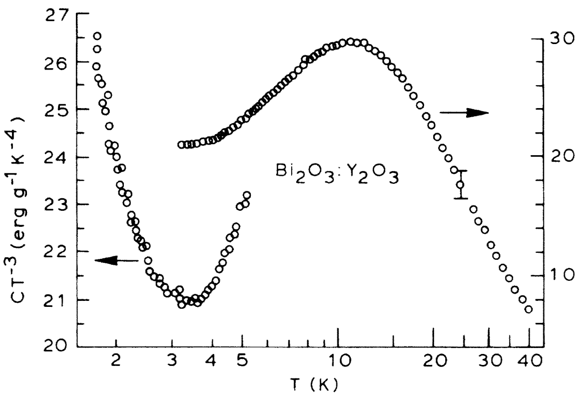

FIG. 1. Specific heat of Bi_2O_3:Y_2O_3 plotted as C/T^3 to illustrate the non-Debye behavior. The uncertainty in the absolute temperature increases above 20 K, and a typical error bar in C/T^3 is shown at 25 K. The maximum in C/T^3 at 12 K is describable by an Einstein term due to the dispersionless mode of the diffusing ions. The rapid rise of C/T^3 below 4 K is due to a linear tunneling term.

III. ANALYSES

Following the results obtained on the other ionic conductors mentioned above, we assume the specific-heat data of Fig. 1 can be decomposed into a linear tunneling term and an Einstein term. The data suggest that the Einstein term is effectively frozen out below 3.5 K, and this is easily checked by a rough estimate, as follows: The Einstein temperature Θ_E is approximately $5T'$, where T' is the

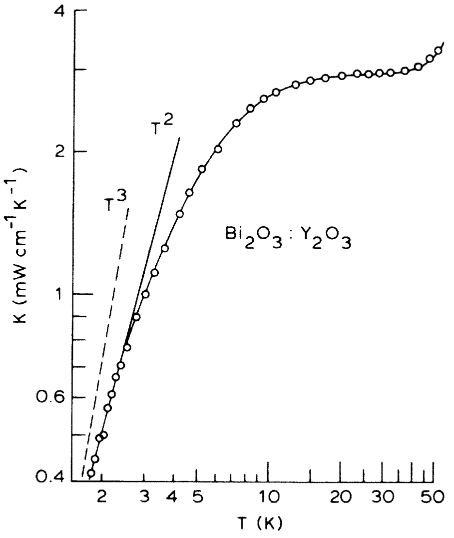

FIG. 2. Thermal conductivity of Bi_2O_3:Y_2O_3. There is a glasslike plateau around 20 K, and below 3 K, $K \cong 1.2\times10^{-4}T^2$ W cm^{-1} K^{-1}.

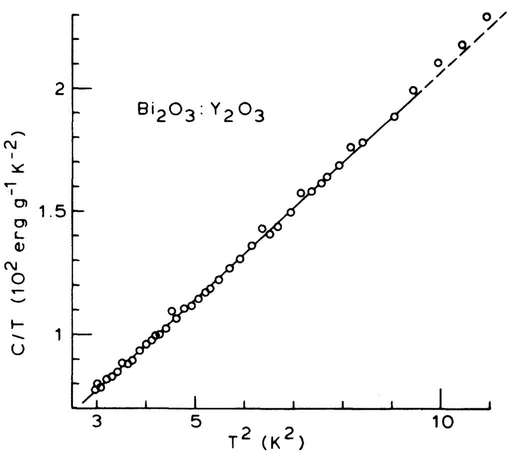

FIG. 3. Fit of the specific-heat data below 3.5 K to the linear tunneling term, Eq. (1). The tail of the Einstein term is present above $T^2=10$ (dashed curve), and these data were not included in the fit. The Debye temperature from this fit is 249.6 K.

temperature of the C/T^3 maximum.[12] Consequently, estimating the amplitude of the Einstein term from the height of the C/T^3 maximum and knowing Θ_E allows an estimate of the Einstein term, and it is found that below about 3.5 K this term is negligible (a subsequent estimate using the parameters from the Einstein fit verified this conclusion). Consequently, the specific-heat data below 3.5 K were fitted to the linear term added to the Debye background[14]

$$C=\alpha T^3+\gamma T\ , \tag{1}$$

where the coefficient α is simply related to the Debye temperature Θ_D and γ is the coefficient of the tunneling term. The result of this fitting is shown in Fig. 3, and an excellent fit to Eq. (1) is obtained. The residual tail of the Einstein term is visible in Fig. 3 above $T^2=10$, and these data were not included in the least-squares fit. The fitting parameters obtained are $\Theta_D=249.6$ K, $\gamma=21.96$ erg g^{-1} K^{-2} $=1.065\times10^{-4}$ cal $mole^{-1}$ K^{-2}. The Debye temperature here is normalized to one atom per formula weight based on the fluorite structure.

There are apparently no literature references with which to compare this fitted Debye temperature. The coefficient of the tunneling term found here is considerably smaller than that found in the β-aluminas. For example, γ varies from 0.5 to 1.7×10^{-3} cal $mole^{-1}$ K^{-2} in the Na, K, Rb, and Li β-aluminas.[2] However, compared to ZrO_2:Y_2O_3, in which $\gamma=3.08\times10^{-5}$ cal $mole^{-1}$ K^{-2}, the tunneling term found here is considerably larger, as is the oxygen-vacancy concentration. We shall return to this tunneling term below.

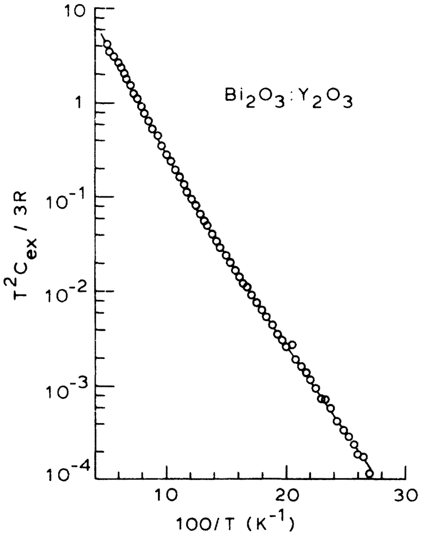

FIG. 4. Fit of the specific-heat data in the neighborhood of the C/T^3 maximum according to the Einstein term, Eq. (2). Here $C_{ex}=C-C_D-\gamma T$, where γ is taken from the Fig. 3 fit. The Debye temperature from this fit is 248.2 K.

Turning next to the (suspected) Einstein term, it is clear from the above fitting parameters that the tunneling term makes a non-negligible contribution above 4 K, so in this range the fitting equation

$$C=C_D(\Theta_D/T)+\gamma T+3Rrx^2e^x/(e^x-1)^2,\quad x=\hbar\omega/kT \tag{2}$$

was used. Here C_D is the Debye function, r is the number of Einstein oscillators per formula weight, and ω is the Einstein frequency. The fitted value for γ was used in Eq. (2), but Θ_D was determined independently. That is, a three-level fitting program was used to determine Θ_D, r, and ω. A tabulation of the Debye function was used,[15] and the results of this fitting are shown in Fig. 4. The fitting parameters here are $\Theta_D=248.2$ K, $\omega=33.1$ cm^{-1}, $r=0.0428$.

An excellent fit to Eq. (2) was found, as seen in Fig. 4; here $C_{ex}=C-C_D-\gamma T$. However, it was found that the Fig. 1 data above 25 K could not satisfactorily be fitted to Eq. (2), and these 25–40 K were *not* included in the fit. A possible reason here may be the relatively large uncertainties in the absolute temperature above about 20 K ($\sim$0.1 K); a typical error bar in C/T^3 at 25 K is shown in Fig. 1. A more likely explanation, however, may be the inadequacy of the simple Debye model applied to a locally disordered solid at temperatures well above the T^3 limit (in this case, temperatures above about 12 K). What is clear, nonetheless, is that the simple models employed here describe the main features of the Fig. 1 data very well, and the agreement between the Debye temperatures determined in the two regions ($\Theta_D=248.9$ K$\pm0.40\%$) lends credence to the fitting procedures. The Einstein frequency found here is in the range of the frequencies in the β-aluminas,[2] 28–82 cm^{-1}, but is approximately one-half the frequency found[6] in ZrO_2:Y_2O_3, 62 cm^{-1}.

The amplitude factor, $r=0.0428$, from the Einstein fit is much *smaller* than the oxygen-vacancy concentration in Bi_2O_3:Y_2O_3 ($\sim50\%$, see above). This is in contrast to the amplitude factors found in the stabilized zirconias. That is, in cubic ZrO_2:Y_2O_3 containing 4.3% oxygen vacancies, $r=0.0492$ (Ref. 6); and in tetragonal ZrO_2:Y_2O_3 containing 1.4% oxygen vacancies, $r=0.0148$.[10] It is clear that the increased oxygen conductivity at elevated temperatures of Bi_2O_3:Y_2O_3 compared to ZrO_2:Y_2O_3 (see above) is due to the large concentration of oxygen vacancies. But at low temperatures the number of diffusing ions contributing to the dispersionless Einstein mode in Bi_2O_3:Y_2O_3 is about the same as in the zirconias. This result suggests an ordering amongst the majority of the vacancies in Bi_2O_3:Y_2O_3 at low temperatures, but this ordering temperature is well above 40 K.

IV. DISCUSSION

The phenomenological model[1] of amorphous materials assumes that groups of ions reside in a double-well potential giving rise to two-level systems, and the density of states for small energies must be nearly constant to reproduce the linear term in the specific heat. However, a *microscopic* description of these low-lying excitations in glasses has not yet been achieved. Consequently, studies of fast-ion conductors are of interest not only because they display glasslike behavior at low temperatures but also because microscopic information about these solids is available. Hopefully, studies of these materials will provide insights into the microscopic nature of glasses. We remark in this regard that certain stochiometric ferroelectrics also display these glasslike properties.[16]

The Bi_2O_3:Y_2O_3 conductor studied here displays classic, glasslike thermal properties over the temperature ranges involved, and the magnitude of the coefficients are very similar to those found in glasses. At elevated temperatures, this defect-fluorite conductor has an oxygen-vacancy concentration an order of magnitude larger than in the stabilized zirconias (as evidenced by the ionic conductivity) and represents a highly disordered state similar to the β-aluminas. In the latter materials, the conduction planes contain 15—30% excess cations plus a corresponding number of charge-compensating oxygens and so are highly disordered. However, in contrast to the zirconias, the Einstein term in the specific heat of Bi_2O_3:Y_2O_3 indicates that the majority of the oxygen vacancies are *ordered* at low temperature and do not contribute to the dispersionless mode resulting from the diffusing ions.

The lower Einstein frequency found in Bi_2O_3:Y_2O_3 (33.1 cm^{-1}) compared to the zirconias (62 cm^{-1}) may simply be due to the more open fluorite structure resulting in more loosely bound oxygen ions. That is, the oxygen-oxygen separation in Bi_2O_3:Y_2O_3 is 2.75 Å compared to 2.55 Å in ZrO_2:Y_2O_3. This difference more than compensates for the difference in ionic radii between Bi^{3+} (1.25 Å) and Zr^{4+} (0.98 Å).[17]

Turning to the linear term in the specific heat, it is here that microscopic information about the solid itself applies. The basic model is that of a periodic host-lattice potential whose wells are partly filled by the interacting, diffusing ions. Theoretical studies[18] of the disorder due to diffusing ions in a periodic potential have demonstrated, however, that this does *not* lead to the linear term; rather, additional random fields due to the mobile ions and the compensating defects are required. A probabilistic theory along this latter line has been given by McWhan *et al.*,[2] according to which

$$\gamma=(\pi^2/6)k^2P(0)x \ , \tag{3}$$

where

$$P(0)=0.11[(e_1^2a/\epsilon)(n_1+e_2^3n_2/e_1^3)^{2/3}]^{-1} \ . \tag{4}$$

Here $P(E)$ is the probability distribution that the energy difference between accessible sites is E, and x is the number of different configurations per oxygen vacancy. In Eq. (4) n_1,e_1 and n_2,e_2 are the concentration and charge of the oxygen vacancies and compensating ions, respectively, ϵ is the dielectric constant, and a is the distance between accessible sites in the unit cell. This formalism is in reasonably good agreement with the linear term observed in the β-aluminas[2] and in ZrO_2:Y_2O_3. For the case of Bi_2O_3:Y_2O_3, there are eight crystallographically equivalent oxygen sites in the fluorite unit cell; the x-ray data yield $a=2.75$ Å, and a measurement of the dielectric constant at helium temperatures yielded $\epsilon=15.4$. There are no charge-compensating ions in Bi_2O_3:Y_2O_3 (i.e., $n_2=0$) in contrast to ZrO_2:Y_2O_3. Concerning n_1, we shall adopt the concentration of mobile vacancies resulting from the Einstein term, 0.0428 vacancies per molecule or $n_1=1.03\times10^{21}$ cm^{-3} using the x-ray density (8.13 g/cm^3). Substituting in Eqs. (3) and (4), $\gamma=20.8$ $erg\,g^{-1}\,K^{-2}$, which is in very good agreement with the experimental value, $\gamma=22.0$ $erg\,g^{-1}\,K^{-2}$. Finally, the density of tunneling states $P(E)$ at $E\rightarrow0$ is 1.05 states/eV from Eq. (4) which is about intermediate between the β-aluminas ($\cong$0.7 states/eV) and ZrO_2:Y_2O_3 (1.2 states/eV).

In conclusion, we find a satisfying agreement and internal consistency between the Einstein and linear terms in the specific heat of Bi_2O_3:Y_2O_3. Not only are the Debye temperatures determined in the two regions in good agreement, but the use of the oxygen-vacancy concentration from the Einstein term in the probabilistic theory of McWhan *et al.* yields good agreement with the measured linear coefficient. It would be worthwhile to extend these measurements on Bi_2O_3:Y_2O_3 into the mK temperature range.

ACKNOWLEDGMENTS

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[1] See the review by W. A. Phillips, J. Non-Cryst. Solids 31, 267 (1978).

[2] D. B. McWhan, C. M. Varma, F. L. S. Hsu, and J. P. Remeika, Phys. Rev. B 15, 553 (1977).

[3] A. S. Barker, Jr., J. A. Ditzenberger, and J. P. Remeika, Phys. Rev. B 14, 4254 (1976).

[4] P. J. Anthony and A. C. Anderson, Phys. Rev. B 14, 5198 (1976).

[5] As early as 1899, Nernst observed oxygen conductivity in a 9-wt. % Y_2O_3—stabilized zirconia [W. Nernst, A. Elecktrochem. 6, 41 (1899)].

[6] W. N. Lawless, Phys. Rev. B 21, 585 (1980).

[7] W. N. Lawless, Phys. Rev. B 22, 3122 (1980).

[8] D. A. Ackerman, D. Moy, R. C. Potter, A. C. Anderson, and W. N. Lawless, Phys. Rev. B 23, 3886 (1981).

[9] T. K. Gupta, J. H. Bechtold, R. C. Kuznicki, L. H. Cadoff, and

B. R. Rossing, J. Mater. Sci. 12, 2421 (1977); T. K. Gupta, Sci. Sinter. 10, 205 (1978).

[10] W. N. Lawless and T. K. Gupta (unpublished).

[11] M. J. Verkerk and A. J. Burggraaf, J. Electrochem. Soc. 128, 75 (1981); T. Takahashi and H. Iwahara, Mater. Res. Bull. 13, 1477 (1978), and references contained therein.

[12] W. N. Lawless, Phys. Rev. B 14, 134 (1976).

[13] W. N. Lawless, Cryogenics 15, 273 (1975).

[14] Other specific-heat functions (Schottky, Einstein, etc.) were attempted, but these fits were vastly inferior to the Eq. (1) fit.

[15] E. S. R. Gopal, *Specific Heats at Low Temperatures* (Plenum, New York, 1960).

[16] I. Henning, P. Frach, E. Hegenbarth, and V. I. Fritsberg, Phys. Status Solidi 70, K7 (1982); W. N. Lawless, Ferroelectrics 43, 223 (1982).

[17] The oxygen ions in the fluorite structure form a simple cubic lattice with the cation at the cube center. The difference in cube diagonals here is 0.35 Å whereas the difference in the cation radii is 0.27 Å.

[18] L. Pietronero, W. R. Schneider, and S. Strässler, Phys. Rev. B 24, 2187 (1981).