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Depressed thermal conductivity of mechanically alloyed nanocrystalline 10 mol% yttria-stabilized zirconia

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Abstract

We present the results of thermal conductivity measurements on bulk nanocrystalline 10 mol% yttria-stabilized zirconia (10 mol% YSZ) in the temperature range between 173 and 773 K. The samples studied in this work, with grain sizes from $d = 17$ nm to $d \approx 1\mu\text{m}$, were obtained by cold compaction and sintering of mechanically alloyed powders. A strong grain-size dependent reduction of the thermal conductivity is observed. We will discuss our results in terms of two different models: i) the Kapitza thermal resistance model, which considers the low thermal conductivity as an effect of the thermal contact resistance at grain boundaries, and ii) the phonon hopping model, based on localization of short wavelength phonons due to enhanced scattering at grain boundaries.

1. Introduction

The improvement of thermal barrier coatings (TBCs) for combustors and turbine blades in gas turbine engines, which would enable them to operate at higher temperatures, is essential to increase their overall efficiency [1, 2]. TBCs are thick films of a refractory ceramic material that protect the metal from the high gas temperature. Yttria-Stabilized Zirconia (YSZ) is the standard material used in high temperature thermal barrier coatings technology, due to its good chemical

stability and excellent thermal and mechanical properties [3]. The prospect of improving even more its performance is the reason of the interest in studying the thermal transport properties of nanostructured YSZ [4, 5]. In dielectric materials the principal way of conductive heat transfer is through acoustic phonons. The kinetic theory establishes that thermal conductivity κ can be expressed in the form:

$$\kappa = \frac{1}{3} C_V v l \quad (1)$$

where C_V is the specific heat at constant volume, v is the sound speed and l is the phonon mean free path [6]. The low thermal conductivity of YSZ, even in single-crystalline samples, is due to the strong phonon scattering by the oxygen vacancies, characteristic of its fluorite structure, resulting in a reduced mean free path [7]. A straightforward strategy to decrease even more the thermal conductivity of thermal insulators consists in introducing into their structure a sufficiently high density of point defects, so that they cause inelastic phonon scattering, thus decreasing the phonon mean free path and the thermal conductivity. A possible alternative is to reduce the grain size down to the nanocrystalline scale. For grain sizes smaller than the phonon mean free path a significant reduction of the thermal conductivity is naturally expected [8]. On the other hand, for grain sizes well in the nanometer range, the additional thermal scattering due to grain boundaries can give rise to a noticeable thermal resistance, the so-called Kapitza resistance [9]. Other authors have interpreted the low values of thermal conductivity in nanostructured insulators as a result of localization of short-wavelength phonons inside the grains. In this model, the thermal transport occurs by phonon hopping through grain boundaries (the phonon hopping model) [10].

In this work we present an experimental study of the thermal conductivity dependence on the grain size in mechanically alloyed 10 mol% YSZ nanocrystalline samples. Assuming that thermal transport is determined by scattering at grain boundaries, we will compare the results of two alternative analyses mentioned above: i) the Kapitza thermal resistance model (KRM), and ii) the phonon hopping model (PHM).

2. Experimental details

Compact 10 mol% YSZ samples with different grain sizes were obtained by cold uniaxial compaction and two steps sintering [11] of mechanically alloyed powders. More details about the compaction and sintering procedures can be found in reference [12]. In this work we study a set of four samples with grain sizes in the nanometer range. An extra microcrystalline sample was

obtained by means of a conventional sintering process. A complete X-ray diffraction analysis using the Warren-Averbach method (W.A.) was carried out in order to confirm the fluorite structure corresponding to YSZ and to obtain information about grain sizes for the nanocrystalline samples [12]. Atomic Force Microscope experiments were performed in tapping mode with silicon cantilevers (nominal radius of 10 nm) in ambient conditions with a Nanoscope IIIa equipment (Veeco). These measurements allowed us to obtain the grain size of the microcrystalline sample and confirmed the grain sizes values obtained from the W. A. analysis. The density of the compact samples was determined using the Archimedes method, with water as fluid. Information about sintering temperatures, densities and grain sizes for each sample is summarized in table I.

The thermal conductivity κ of each sample was determined from separate measurements of the thermal diffusivity α , specific heat C_p , and density ρ , using the relationship

$$\kappa = \alpha C_p \rho \quad (2)$$

Thermal diffusivity was measured with a commercial Anter Flashline 3000 system. All samples were covered with a graphite screen to ensure full absorption of the flash light at the front surface and highest emissivity from the backside. Thermal diffusivity was measured from 173 K to 773 K in inert atmosphere. Several measurements were performed under the same conditions to check that there were no changes in samples or damage of the graphite screen during the experiment. Thermal diffusivity values were obtained from the raw data by applying the Clarke and Taylor correction [13], which takes into account radiative losses that occur in nonadiabatic conditions. Heat capacity was measured between 173 K and 773 K with a Netzsch Jupiter 404 Differential Scanning Calorimeter (DSC), using platinum crucibles in helium atmosphere. A single crystalline sapphire sample was used as reference. The thermal conductivity values were corrected to account for the porosity, $P = 1 - \rho / \rho_{theor}$, using the relation proposed by Klemens [14]:

$$\frac{\kappa_{porous}}{\kappa_{dense}} = 1 - \frac{4}{3} P \quad (3)$$

3. Results and Discussion

In first place, we will describe the microstructure of the five samples studied in this work. Accurate determination of grain sizes is not an easy task for nanocrystalline materials. The simple but very common analysis of XRD patterns in terms of Scherrer relation can lead to underestimated grain size values. For that reason we have performed careful X-ray profile analyses, and checked the results with those obtained from AFM images. The samples obtained by cold com-

paction and two steps sintering of the mechanically alloyed powders display grain sizes d ranging from the 17 nm (green sample) to about 100 nm (see table I), as determined from a Warren-Averbach line profile analysis of X-ray diffraction patterns [12]. Atomic Force Microscope (AFM) experiments were performed in order to confirm these values. In Figure 1 we show a typical AFM image of the sample with $d = 53$ nm from XRD. The figure displays a uniform and isotropic distribution of grain sizes around an average value $d = 50 \pm 3$ nm, as deduced from treatment of images using WSxM2.2 software from Nanotec [15], in very good agreement with the value obtained from XRD analysis. In the case of the microcrystalline sample, the grain size cannot be obtained from X-ray analysis, and $d \approx 1 \mu\text{m}$ was determined from AFM images. The images reveal relatively low porosity, consistent with the density values, higher than 90 % of the theoretical X-Ray density ($\rho_{\text{theor}} = 5.93 \text{ g cm}^{-3}$), except in the case of the sample with smallest grain size, 17 nm, that shows $\rho \approx 84 \% \rho_{\text{theor}}$.

As we have already mentioned the thermal conductivity κ values were calculated from specific heat, diffusivity and density measurements. In figure 2 (a) we present temperature dependence of molar specific heat C_p between 173 K and 773 K for each sample. The specific heat points reach a value higher than that predicted by Dulong and Petit law ($72.75 \text{ J mol}^{-1}\text{K}^{-1}$) at high temperature. Moreover, the values present a slightly positive slope instead of reaching the expected plateau. This phenomenon has been reported in previous works for this material [16]. The authors interpreted this result as a possible contribution of lattice defects to the specific heat. On the other hand, the observed differences between the C_p values of our samples are smaller than the equipment accuracy, $\pm 3\%$, included as error bars in figure 2 (a). Thus, we can conclude that C_p does not depend significantly on grain size, at least for 10 mol% YSZ samples with grain sizes varying from the micrometer range down to 17 nm. In figure 2 (b) we display thermal diffusivity α as a function of temperature between 173 K and 773 K, for all the samples studied in this work. In contrast to specific heat, in this case we do observe a clear grain size dependence of thermal diffusivity, which strongly decreases with decreasing grain size. In the case of the microcrystalline sample, the diffusivity values are more than two times higher than those corresponding to the nanocrystalline samples.

In figure 3 we show the temperature dependence of thermal conductivity κ between 173 K and 773 K for the samples studied in this work. As explained above, the raw data were corrected in order to take into account the sample's porosity. For this purpose, different corrections formulas can be found in the literature. In our case, as different methods render similar results, we decided to use the usual Klemens relation [14, 17]. The thermal conductivity shows weak temperature dependence above $T \sim 400$ K, tending to saturate at a constant value at high temperature. On the other hand, as it is observed for diffusivity measurements, κ is strongly depen-

dent on grain size. All the nanocrystalline samples display a significant reduction of thermal conductivity values respect to that of the microcrystalline sample.

As a matter of fact, these κ values are lower than the reported theoretical values calculated using an Einstein model for disordered crystals [18]. Similar results in YSZ thin film samples [19], polycrystalline alloys [20] and compounds [21, 22] have been previously reported and tentatively explained by different authors as a consequence of a higher additional thermal resistance due to contact between grain boundaries, the so called Kapitza resistance. For polycrystalline materials, values of Kapitza resistance can be obtained from κ values measured as a function of grain size [22] using the following expression:

$$\frac{1}{\kappa} = \frac{1}{\kappa_0} + \frac{R_K}{d} \quad (4)$$

where R_K is the Kapitza resistance, d is the grain size and κ_0 is the conductivity that correspond to the single crystal. Nan and Birringer [20] used an effective medium approach to develop a similar relationship. In the present study, we have used (4) to obtain the Kapitza resistance (R_K) and bulk conductivity (κ_0) from fits of $1/\kappa$ versus $1/d$. In figure 4 we display these fits for different temperatures. Only the experimental points corresponding to the microcrystalline sample ($d = 1 \mu\text{m}$), which exhibit a clear deviation from the linear alignment of the rest of the data, have not been included in the fits. We want to point out that, using analogous analyses, other authors have observed the same trend, that is, the analysis in terms of a constant R_K is valid only for the nanocrystalline samples [21, 22]. The R_K values obtained for our YSZ nanocrystalline bulk samples are displayed in figure 5 (a). The Kapitza resistance R_K decreases with increasing temperature, approaching a plateau at $R_K = 9.5 \cdot 10^{-9} \text{ (m}^2\text{K/W)}$ for $T > 350$, of the same order than previously reported values [19, 23]. In figure 5 (b) we present the κ_0 values obtained from fits of $1/\kappa$ versus $1/d$ to expression (4) for different temperatures. These κ_0 are significantly lower than those from literature and than $\kappa(T)$ for our own microcrystalline sample. As a result of the same type of analysis of their data for nanocrystalline YSZ thick coatings, Yang et al. [19] obtained also reduced κ_0 values, what they interpreted as a consequence of the reduced grain size. However, it is necessary to point out that, although the previous analysis in terms of Kapitza resistance at grain boundaries seems fairly satisfactory, it is based on hypotheses and approximations that can be considered, at least, somewhat crude. It has been suggested, for example, that theoretical treatments based on the validity of Fourier equations could break down for grain sizes well in the nanometer scale, similar to the phonon wavelength [19, 24]. In that case, it is also doubtful that thermal transport could be described in terms of coherent movement of phonons through the lattice [10].

To explain the peculiarities of high temperature heat transport in nanocrystalline and porous materials, Braginski et al. proposed an alternative model, based on phonon hopping through grain boundaries [10]. In the framework of the PHM, $\kappa(T)$ for a given material can be calculated using the following expression:

$$\kappa(T) = k_B T \int_0^{1/\theta} \frac{\kappa_i B(x) t \bar{S} \Phi}{\hbar k_B^{-1} \kappa_i a^2 d + k_B T_D B(x) t \bar{S} \Phi} dx \quad (5)$$

being

$$B(x) = \frac{9}{2} \theta^4 \frac{x^4 e^x}{(e^x - 1)^2} \left(x - \frac{1}{\theta} \right)^2.$$

The other parameters in expression (5) are: κ_i , the conductivity of single-crystal YSZ, d the grain size, T_D the Debye temperature, $\theta_D = T/T_D$, a is the lattice parameter, S the main area of interface, Φ is a factor relevant to the disorder, and t is the unique fitting parameter, which describes the interface transparency for the phonon hopping. The different lines in figure 3 are fits to this expression for the high temperature data ($T \geq 300$ K), using $T_D = 650$ K, estimated from our specific heat measurements (see figure 2 (a)), in good agreement with the results obtained for YSZ by other authors [25, 26]. We have used $\kappa_i = 2.2$ W/mK for the intrinsic thermal conductivity of 10 mol% YSZ in this temperature range. In the fits to expression (5), the grain boundary transparency t is the only free parameter. It is important to remark that t is much higher for the microcrystalline sample, which has been also observed in other systems [27]. It has been proposed that, in practice, the Kapitza analysis is a limit of the PHM, and that t is proportional to the Kapitza conductance [28]. Besides of this, it can be considered that, compared to the simple analysis in terms of a phenomenological constant Kapitza resistance, the PHM describes the interfacial thermal resistance in terms of phonon localization induced by the enhanced phonon scattering at grain boundaries.

An interesting possibility is that this phonon localization effect might be due to changes in vibrational anharmonicity induced by grain size reduction. As a matter of fact, in glasses and in disordered crystals it has been proposed that vibrational anharmonicity might regulate both the thermal conductivity [29] and ultrasonic attenuation for $T > 100$ K [30, 31], although there is some controversy about the issue [32]. The possibility suggested above seems quite reasonable, because even for single crystal YSZ the thermal conductivity below room temperature and the *low temperature* specific heat ($T < 10$ K) exhibit features typical of glassy systems [33, 18]. Thus, low temperature specific heat and thermal conductivity measurements on the present samples are desirable for a better understanding of the thermal properties in this system.

From the theoretical point of view, a marked grain size effect on the thermal conductivity is naturally expected [7, 10]. Klemens and Gell have demonstrated a reduction up to 60% for a grain size of 10 nm in 7%wt YSZ. On the other hand, from the experimental point of view, there is some controversy about the existence of this grain size effect on the thermal conductivity of YSZ. It is important to point out that our work has been performed on bulk isotropic nanocrystalline samples. Previous works, showing similar but not so patent grain size effects, were performed on nanocrystalline YSZ coatings [4, 19] that usually display columnar structure, which could explain their higher conductivity values. On the other hand, Raghavan et al. have discarded the effect of the grain size, proposing instead that the reduction of thermal conductivity is only a consequence of the porosity effect in bulk nanocrystalline samples [5]. But they only discard grain size effects *above* 100 nm. As a matter of fact, their results show a depressed thermal conductivity for $d \leq 100$ nm. In any case, our analysis indicates that the extremely low thermal conductivity observed in our samples is a genuine grain size effect.

4. Conclusions

In this work we present the results of thermal conductivity measurements on a set of samples, with grain sizes between 17 nm and 1 μm . We observe a substantial reduction in thermal conductivity respect to the bulk values. Two alternative analyses in terms of the Kapitza resistance and the phonon hopping models allow us to conclude that there is a genuine grain size effect on the thermal conductivity in nanocrystalline YSZ. It is quite reasonable to interpret our results in terms of a phonon localization effect could be related to changes in vibrational anharmonicity.

The results reported in this work could open the possibility of technological applications in the field of high temperature thermal barrier coatings, if a way of impeding grain growth to preserve the nanometric grain size were found.

Acknowledgements

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TABLE

Table 1 Sintering temperatures used in two step method, density, grain sizes obtained using Warren-Averbach method, and the grain boundary transparency parameter t .

Sintering Temperature		Density	Grain size	t
T_1 (°C)	T_2 (°C)	(% theoretical)	(nm)	
1350	1350	93.0 ± 0.2	~1000	0.2870
1150	950	92.7 ± 0.2	104	0.0034
1050	850	91.2 ± 0.2	53	0.0055
950	750	90.7 ± 0.2	29	0.0084
Green sample		84.0 ± 0.5	17	0.0120

FIGURE CAPTIONS

Figure 1. Atomic Force Microscope Image ($500 \times 500 \text{ nm}^2$) for the sample with 53 nm grain size.

Figure 2. (a) Molar specific heat C_p and (b) thermal diffusivity α of 10 mol% YSZ samples studied in this work as a function of temperature. Different symbols correspond with samples with different grain-size. Errors bars ($\pm 3 \%$ for C_p and $\pm 5\%$ for α) are included in both cases. Solid line is a Debye function with $T_D=650 \text{ K}$.

Figure 3. Temperature dependence of thermal conductivity κ for the samples studied in this work. Lines are the results of fits to expression (5) (phonon hopping model[10], see text). Error bars for κ ($\pm 8\%$), are included.

Figure 4. κ^{-1} vs. d^{-1} plots for different temperatures. The points are experimental data while the solids lines are fits of the experimental data to equation (4), excluding the points corresponding to $d = 1 \mu\text{m}$ which show a clear discrepancy.

Figure 5. (a) Kapitza resistance, R_k , and (b) values of κ_0 , obtained from the fits of our experimental data to equation (4) shown in figure 4.

Figure 1

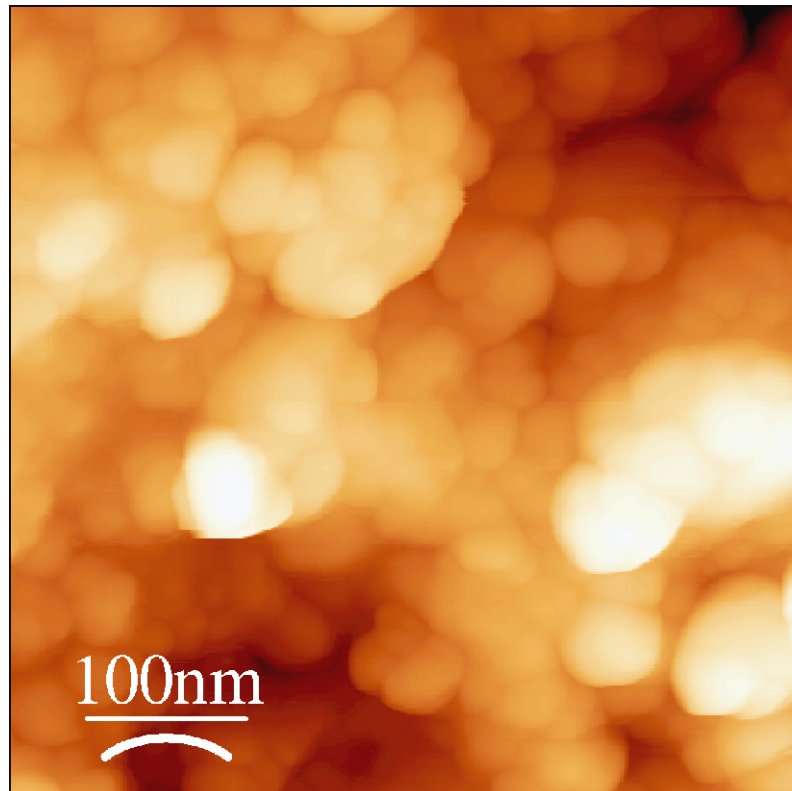


Figure 2 (a)

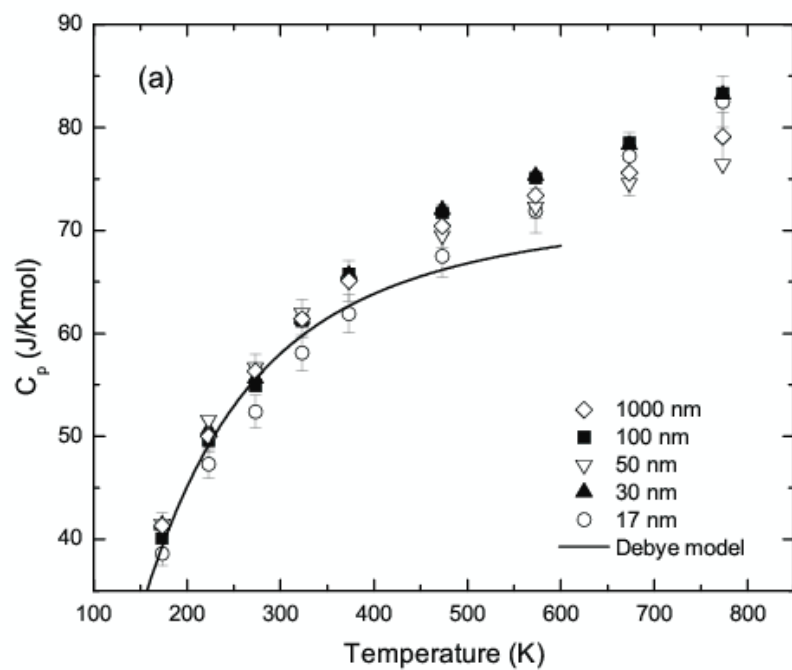


Figure 2 (b)

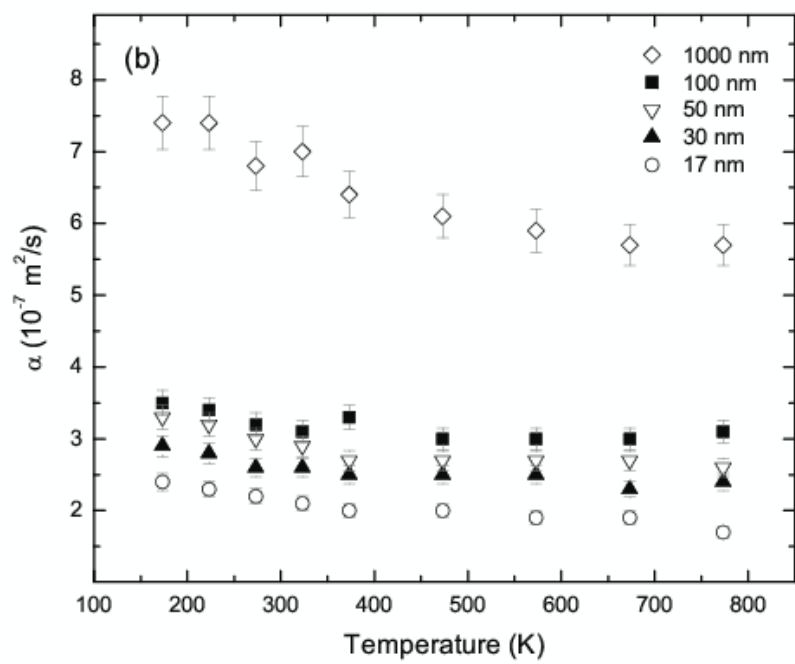


figure 3

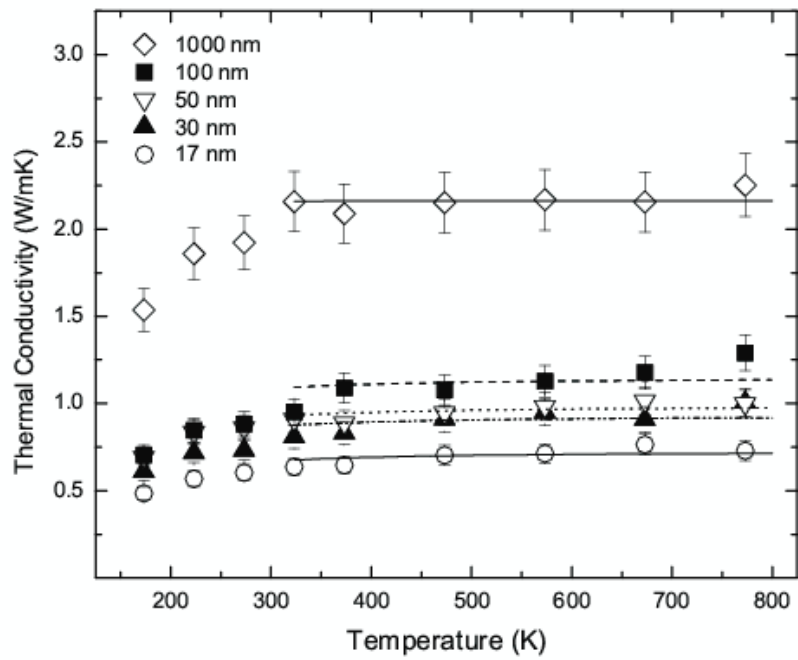


figure 4

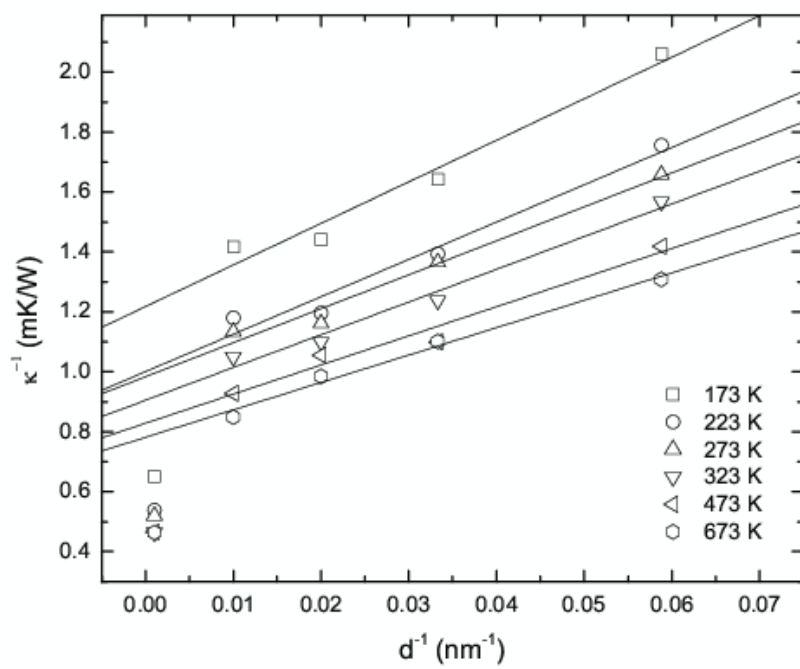


figure 5 (a)

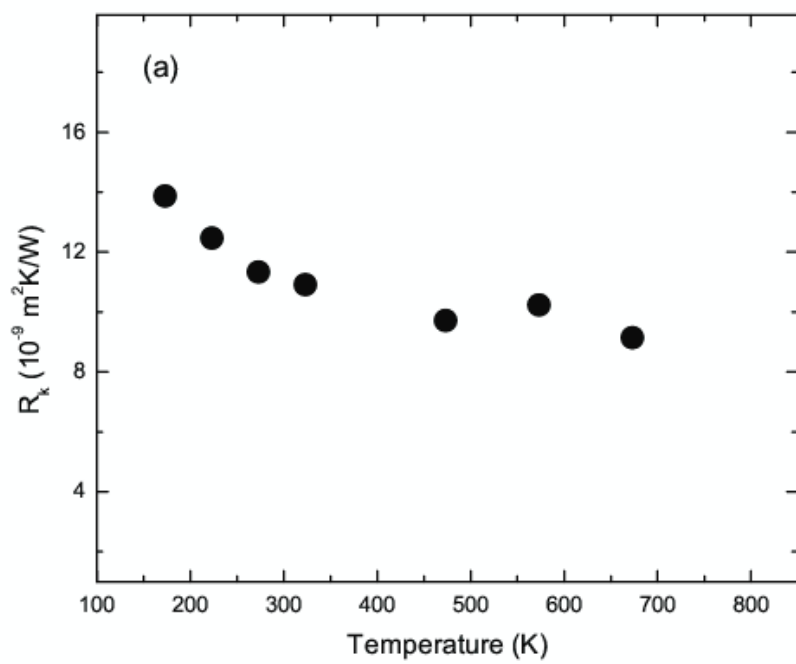


figure 5 (b)

