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Influence of grain size on the thermal conductivity of tin oxide ceramics

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Abstract

Measurement of the thermal diffusivity by the laser flash technique has been used to evaluate thermal conductivity values between 20°C and 900°C for tin oxide ceramics. By using MnO_2 as a sintering additive, strong variation of the microstructure in terms of porosity and average grain size was achieved in the samples. For dense ceramics, larger average grain size yielded a significant increase in the room temperature thermal conductivity. This could be attributed to a reduction of the number of grain boundaries in the heat flow path. The grain boundary interfacial resistance was consequently estimated at 4.1×10^{-8} m^2 KW^{-1}. Data concerning the effects of additive amount, pore content, and temperature are also reported.

Keywords: Tin oxide; Thermal conductivity; Microstructure-final; Grain size; SnO_2

1. Introduction

In solid oxides heat is predominantly carried by lattice vibrations. The thermal conductivity is generally observed to decrease with temperature in the range 0–1000°C. This is explained by greater mutual scattering of the vibrational waves through Umklapp processes which shortens the mean free path.[1] For polycrystalline materials, microstructural factors can also have a significant influence on the measured thermal conductivity of a sample. Pores, filled with gas of a lower thermal conductivity than the solid phase, help block the heat flow and thus make the material more insulating. Interfaces such as the solid–solid grain boundaries, which are crossed by the heat flow path, can also inhibit heat conduction. For the low temperature range, where the mean free path is limited by the crystallite dimensions, strong decrease in thermal conductivity has been shown in small grain Si–Ge alloys compared to larger grain material.[2] At higher temperatures, where the mean free path becomes considerably smaller than the crystallite dimension, in some materials the grain boundaries have been shown to have little role. For example, Kingery and Charvat reported no difference in the values of thermal conductivity above 200°C for Al_2O_3 in single crystal form or in polycrystalline form.[3] However, the nature and influence of grain boundaries is not necessarily the same in all materials. It is possible that additional thermal resistance can be attributed to the localized region of the grain boundary in a manner which is distinct from the response of the bulk of a grain. Furthermore there are not many studies of the role of grain boundaries in the thermal conductivity, even for the relatively accessible temperature range of 20–1000°C. We, therefore, report thermal conductivity values for tin oxide ceramic samples where the pore content and grain size have been varied. The data were obtained via measurement of the thermal diffusivity between room temperature and 900°C.

Tin oxide (SnO_2) was chosen as a model system for the study of the influence of microstructural variation because of previous experience gained in our laboratory with respect to its preparation. In particular a sintering additive (MnO_2) has been used to achieve a wide range of porosities and then grain sizes in the case of dense ceramics.[4,5] Other advantages of tin oxide are that it is a single phase material, the thermal expansion is only slightly anisotropic[6] which means that microcracking problems are avoided, and it has a fairly high thermal

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conductivity, above 30 Wm^{-1} K^{-1} at room temperature.[7] Interface effects are less likely to be obscured than they would be in a more insulating solid or more complex multiphase material. Finally it can be noted that SnO_2 is a technologically important material which has found applications in gas sensors and as transparent electrodes in photovoltaic devices.

2. Experimental

2.1. Sample preparation

Satisfactory densification of pressed powder pellets of SnO_2 cannot be achieved without the use of a sintering additive. MnO_2 (Aldrich) was, therefore, added to 99.9% pure SnO_2 powder (Aldrich, -325 mesh) in amounts of either 0.5, 1, or 2 wt%. The powders were attrition milled for 1 h in ethanol. After removal of the ethanol by evaporation (12 h at 60°C), the powders were thermally treated at 400°C for 4 h. The samples were then pressed uniaxially (50 MPa) without binder into discs of 10 mm in diameter and typically 2.5 mm in thickness.

A first set of samples with variation in the apparent density between 50 and 95% of the theoretical value was obtained by sintering for 12 min at the temperatures given in Table 1. A second set of dense samples with variable grain size was achieved by sintering the 1 wt% MnO_2 powder at 1100°C for different durations (Fig. 1 and Table 2).

2.2. Sample characterisation

The sample densities were evaluated in two ways. All samples had their dimensions measured and were dry weighed. Archimedes' method was also used on the samples containing 1 wt% of MnO_2. Typically the geometrical method gave results slightly lower than Archimedes' method but within 2%. The microstructures were also examined by scanning electron microscopy or by optical microscopy. In particular, the linear intercept method was used to estimate the average grain size of dense ceramics.

The thermal conductivities were evaluated by measurement of the thermal diffusivities using the laser flash technique.[8,9] A Nd - glass laser operating at 1.06 μm is used as the flash source to heat up the front face of a disc shaped sample. The transient back face temperature was monitored with a liquid nitrogen cooled infra-red detector (HgCdTe) connected to an amplifier and a storage oscilloscope. The disc sample dimensions are typically 8 mm in diameter and 2 mm in thickness. From room temperature to 400°C, measurements were made in air and from 500 to 900°C, the measurements were made in vacuum. The temperature–time data was analysed using Degiovanni's method[10] which takes into account the effect of heat losses on the value of thermal diffusivity. The thermal conductivity (λ) is then calculated from the expression

$$\lambda = \rho c \alpha \tag{1}$$

where ρ is the sample density, c is the specific heat, and α is the thermal diffusivity. The specific heat values for the SnO_2–MnO_2 compositions were calculated from thermochemical data[11] using the rule of mixtures with the following polynomial

$$c = (70.835 + 7.598 \times 10^{-3} T - 1.661 \times 10^{6} T^{-2}) \frac{F_{MnO_2}}{M_{MnO_2}} + (66.467 + 16.644 \times 10^{-3} T - 1.674 \times 10^{6} T^{-2}) \frac{F_{SnO_2}}{M_{SnO_2}} \tag{2}$$

where F_{MnO_2}, F_{SnO_2} refer to the weight fractions and M_{MnO_2}, M_{SnO_2} refer to the molar weights of MnO_2 and SnO_2.

3. Results and discussion

3.1. Room temperature measurements

The thermal conductivity values at room temperature for the three series of samples 0.5 wt% MnO_2, 1 wt% MnO_2, and 2 wt%MnO_2, show a steady increase as a

Table 1
Percentage of theoretical density of SnO_2 samples sintered 12 min at different temperatures

0.5% MnO_2		1% MnO_2		2% MnO_2	
Temperature	Percentage of theoretical density	Temperature	Percentage of theoretical density	Temperature	Percentage of theoretical density
1000	51.6	900	55.8	900	53.6
1050	59.7	925	63.4	925	61.4
1075	69.7	950	69.6	950	73.5
1085	75.8	975	77.5	1000	85.3
1100	85.3	1000	83.4	1025	89.5
1150	95.2	1100	92.1	1100	95.8

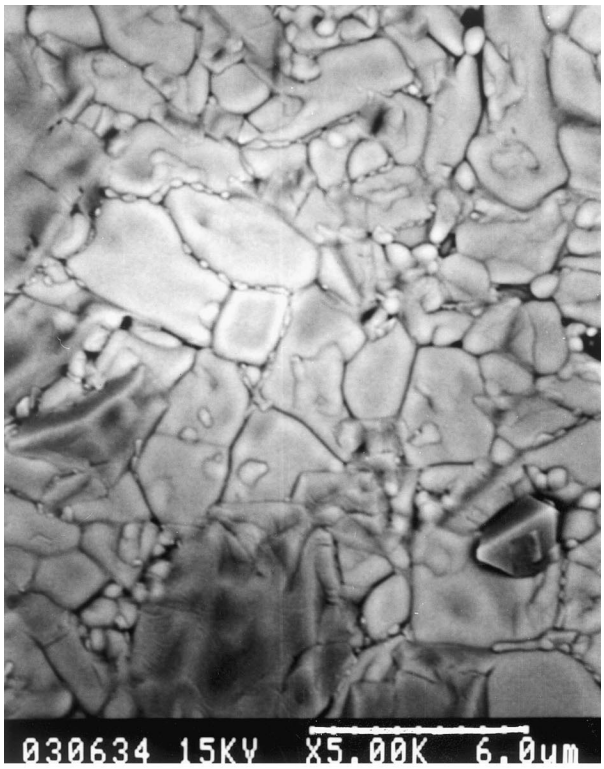

Fig. 1. (a) SEM micrograph of SnO_2 ceramic containing 1 wt% MnO_2 sintered at 1150°C for 12 min. The sample surface has been thermally etched at 1100°C after polishing. (b) Optical micrograph of SnO_2 ceramic containing 1 wt% MnO_2 sintered at 1150°C for 48 h. No surface preparation before observation.

function of density (Fig. 2). The dependence is steeper than that which would be predicted by a Maxwell–Eucken expression,[12] suitable for dispersed spherical pores in a continuous matrix, but it is difficult to take into account pore shape and distribution over such a wide range of porosity. However, from this data, the approximate linear dependence can be used to correct empirically for small porosity variations between samples.

Table 2
Percentage of theoretical density of SnO_2 samples with 1% of MnO_2 sintered at 1100°C for different durations

Sintering time (h)	Percentage of theoretical density (%)	Average grain size (μm)
0.2	92.1	2.4
4	96.4	4.8
24	95.7	6.7
48	96.1	7.8

It can be noted that the amount of sintering additive has little significant effect though the 2 wt% MnO_2 samples seem to be slightly lower in thermal conductivity than the other two series. Recent work by Dos Santos et al., has reported the decrease of thermal conductivity resulting from Nb addition to Al_2O_3.[13] The Nb is assumed to go into the alumina lattice which results in greater scattering of the lattice vibrations. However, an alternative explanation of our data can be put forward. Mn cations are practically insoluble in a lattice of SnO_2. They are deduced to be located at the periphery of the grains, possibly in a segregated layer.[14] Gouvea showed that increasing the MnO_2 content in SnO_2 decreased the grain size when the sintering conditions yielded similar densities.[4,5] The contribution of interfacial thermal resistance to the total thermal resistance of the SnO_2 ceramic would therefore increase. Such a grain size effect on the thermal conductivity was explored further.

Sintering the 1 wt% MnO_2 samples at 1100°C over different durations yielded dense ceramics with average grain size varying from 2.5 μm up to almost 8 μm, Table 2. The corresponding themal conductivities show a marked increase for larger grain size where the number of grain boundaries in the heat flow path is reduced (Fig. 3). A corrected value of 27 $Wm^{-1}\ K^{-1}$ equivalent to 96% relative density can be estimated for the first sample (marked by a cross in Fig. 3). It is then possible to make the following estimate of the grain boundary interfacial thermal resistance, independent of porosity variation. The polycrystalline ceramic is assumed to consist of cubic grains with an edge dimension corresponding to the average grain size. Only the interfaces which are perpendicular to a 1 dimensional heat flow path through the sample between the two faces are considered to present thermal resistance. The first sample, 2 mm thick and 50 mm^2 in cross-section, has a thermal resistance of 1.48 KW^{-1} and with an average grain size of 2.4 μm contains 833 interfaces. The second sample of similar dimensions has a thermal resistance of 1.14 KW^{-1}. The average grain size of 4.8 μm corresponds to 417 interfaces. The additional 416 interfaces in the smaller grain size sample therefore increase the thermal resistance by 0.34 KW^{-1}. The interfacial thermal resistance of a grain boundary, independent of its surface area, is thus estimated to be $4.1\times10^{-8}\ m^2\ KW^{-1}$.

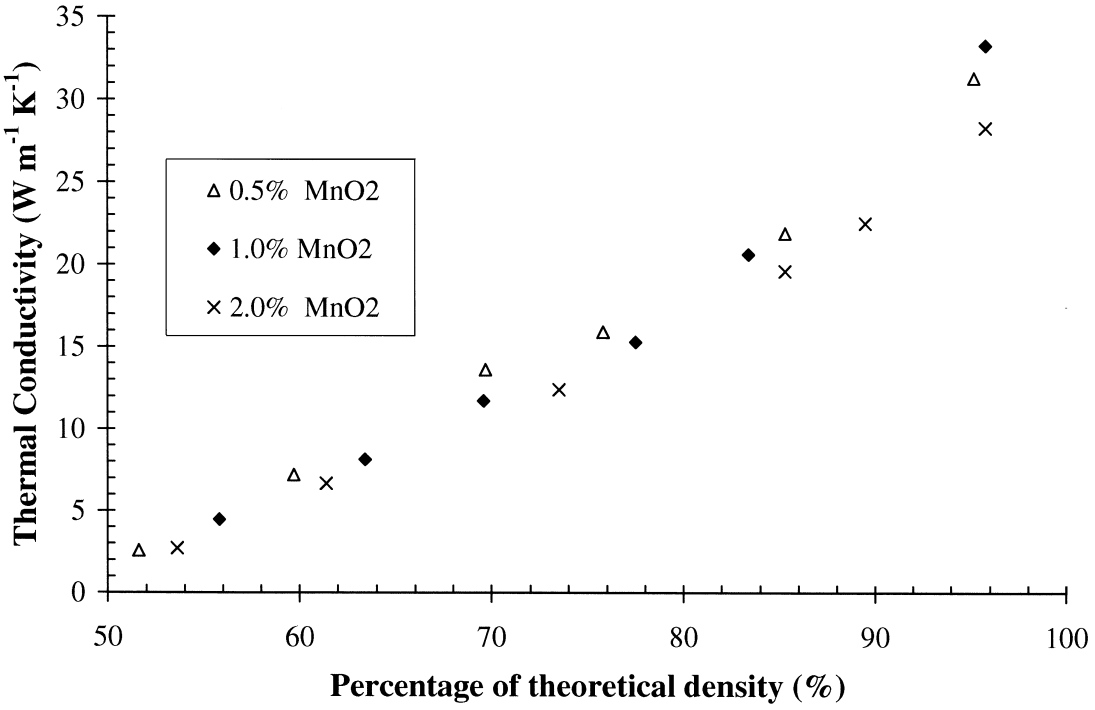

Fig. 2. Thermal conductivity at room temperature versus percentage of theoretical density for series of SnO_2 ceramics containing 0.5 wt% MnO_2, 1 wt% MnO_2 and 2 wt% MnO_2.

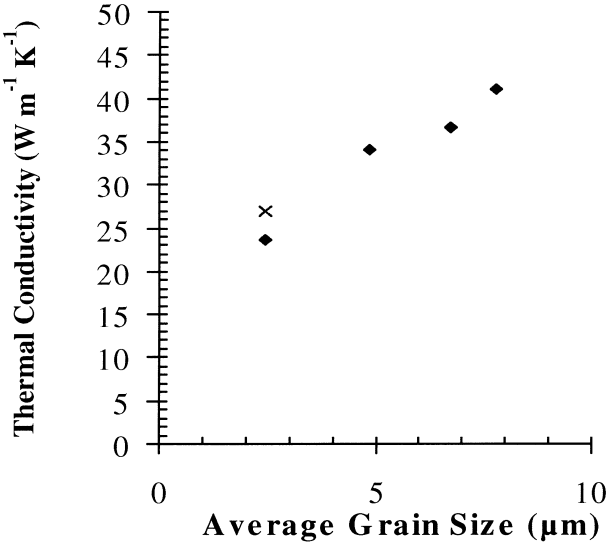

Fig. 3. Thermal conductivity at room temperature versus average grain size for SnO_2 ceramics containing 1 wt% MnO_2 sintered at 1150°C. The cross marks an estimate of the thermal conductivity of the sample sintered for 12 min when the porosity content is corrected to 4% similar to the other samples.

The extrapolation of this result suggests that a single crystal of SnO_2 has a thermal conductivity of 50 Wm^{-1} K^{-1} at room temperature. Comparison can also be made to a recent evaluation of the Kapitza radius for $NiAl/Al_2O_3$ interfaces[15] which is equivalent to a thermal resistance of the order of 10^{-8} m^2 KW^{-1}.

3.2. Medium and high temperatures

Grain boundary scattering of lattice vibrations should have less influence on the thermal conductivity of tin oxide as the mean free path shortens at higher temperatures. Measurements up to 900°C indeed seem to reveal such behaviour (Fig. 4). Above 600°C, the values of thermal conductivity from the four different samples virtually superimpose apart from the smallest grain size sample being just distinguishably the lowest, which can be attributed to its slightly greater pore content. We might deduce that the grain boundary interfacial thermal resistance tends to zero. However, it is worth pointing out that, for a sample with a thermal conductivity of 10 Wm^{-1} K^{-1}, the additional effect of 800 grain boundaries in series (2.5 μm size grains) with an interfacial thermal resistance similar to our estimated value at room temperature, would only decrease the conductivity by 1.5 Wm^{-1} K^{-1}. This is similar to the scatter in the data at 900°C. Thus the increased thermal resistance of SnO_2 (single crystal) at high temperature helps to obscure the grain boundary contribution.

Finally it is interesting to consider the temperature dependence of the diffusivity data for the sample sintered 48 h. Because of the high density and largest grain size, microstructural effects are minimized and this sample approaches most closely the case of a single crystal. We consider the common, though without doubt approximate, expression

$$\lambda = \frac{\rho c v l}{3} \quad (3)$$

where v is the average speed of vibrational propagation and l the mean free path of those vibrations responsible for thermal resistance.[1] If c and v are assumed to be weakly dependent on temperature, then λ is principally controlled by l. Above the Debye temperature the mean free path has a behaviour which should be close to an inverse temperature dependence due to Umklapp scattering of phonons. This can be satisfactorily verified in Fig. 5 above 300°C where λ^{-1} is plotted against temperature and shows linear behaviour.

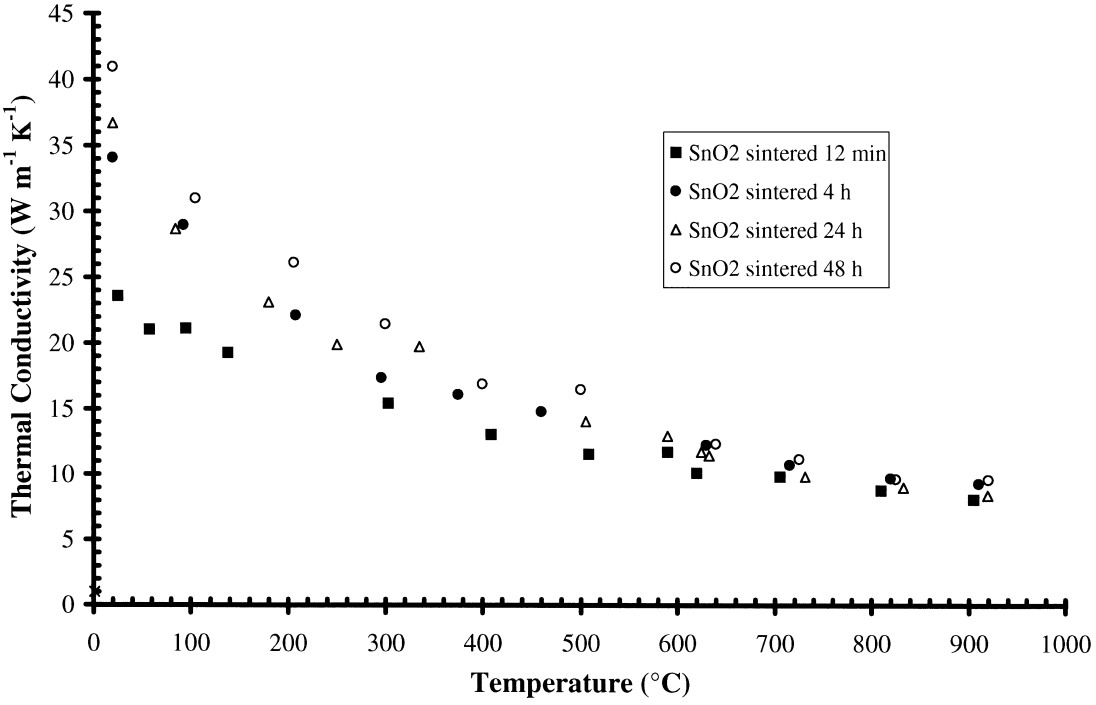

Fig. 4. Thermal conductivity versus temperature for SnO_2 ceramics containing 1 wt% MnO_2 and sintered at 1150°C.

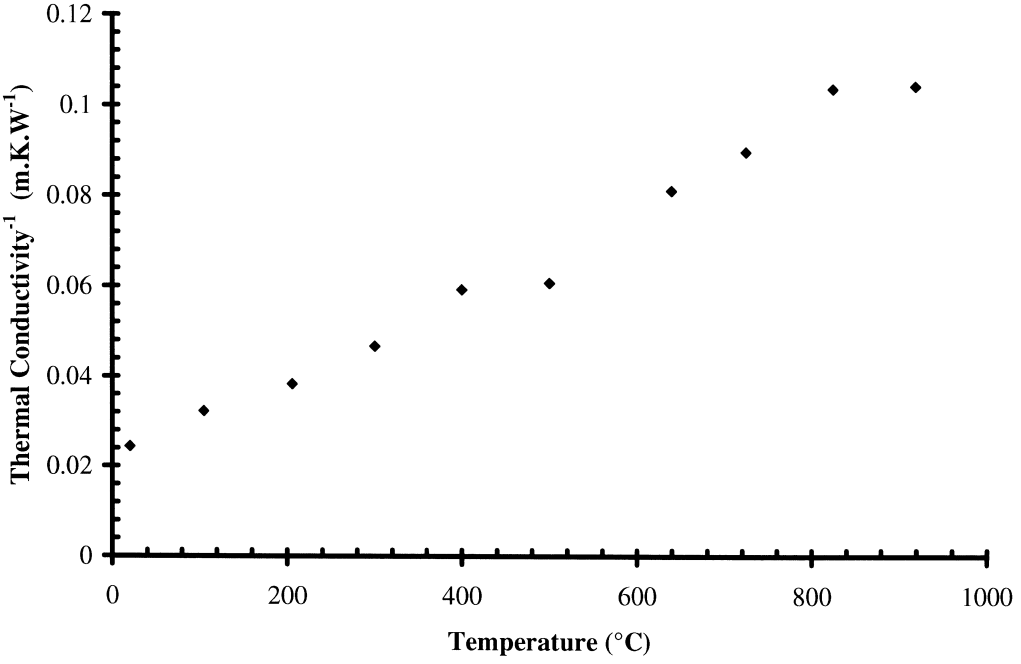

Fig. 5. Inverse thermal conductivity versus temperature for SnO_2 ceramic containing 1 wt% MnO_2 and sintered at 1150°C for 48 h.

4. Conclusions

The influence of microstructural modifications on the thermal conductivity of tin oxide ceramics has been studied. In particular the average grain size of dense samples has been varied through a careful choice of sintering conditions. We have thus been able to show a significant increase in the room temperature conductivity for larger grain ceramic. This can be attributed to the reduction in the number of grain boundaries blocking the heat flow path. The interfacial thermal resistance of grain boundaries in tin oxide is estimated at 4.1×10^{-8} m^2 KW^{-1}.

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