Thermal Conductivity of Al_2O_3 Ceramics: The Inconsistency between Measured Value and Calculated Value Based on Analytical Models for a Composite

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The thermal conductivities of high purity Al_2O_3 ceramic and Al_2O_3 ceramic with ZrO_2 additive were measured by the Laser Flash Method. The measured thermal conductivity was analyzed by the Eucken model for a composite. The measured values were 4 W/mK lower on average than those calculated from this model. Also, there was about a 5 W/mK deviation in the measured value for the same volume of Al_2O_3. It was suggested that the inconsistency and the deviation were caused by the shape of pores and grain boundary phase.

Key words: Thermal conductivity, analytical models and alumina ceramic.

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การนำความร้อนของอะลูมินาเซรามิก: ความไม่สอดคล้องกันระหว่างค่าการนำความร้อนที่ได้จากการวัดและจากการคำนวณโดยใช้โมเดลสำหรับวัสดุเชิงประกอบ

ชิเกทากะ วาดะ บงกช เปี่ยมเพิ่มพูน เปาว์ ณ นคร ธนากร วาสนาเพียรพงศ์ และ
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ค่าการนำความร้อนของอะลูมินาเซรามิกที่มีความบริสุทธิ์สูงและอะลูมินาเซรามิกที่เจือเซอร์โคเนียในสถานะเฟสที่สอง วัดได้โดยวิธีเลเซอร์แฟลช และนำมาวิเคราะห์โดยใช้โมเดลสำหรับวัสดุเชิงประกอบของ Eucken พบว่าค่าที่วัดได้มีค่าต่ำกว่าค่าที่คำนวณได้ประมาณ 4 W/mK โดยเฉลี่ย และมีความเบี่ยงเบนในกลุ่มตัวอย่างที่มีปริมาณอะลูมินาเท่ากันประมาณ 5 W/mK จากผลการทดลอง คาดว่าความไม่สอดคล้องและความเบี่ยงเบนนี้ มีสาเหตุมาจากรูปร่างที่แตกต่างกันของรูพรุน และจากความแตกต่างของปริมาณเฟสของขอบเกรนในแต่ละชิ้นตัวอย่าง

คำสำคัญ การนำความร้อน โมเดลในการคำนวณ อะลูมินาเซรามิก

INTRODUCTION

Since the thermal conductivity of Al_2O_3 is higher than those of many oxides and glasses and it is one of the more popular ceramic materials, it has been widely used for heat sinks and packages in the semiconductor industry and other applications. The thermal conductivity of 96-97% pure Al_2O_3 substrate on the market is about 20-24W/mK. This is not so high when compared with the 40W/mK for pure Al_2O_3.

Commercial alumina ceramics usually include some amount of SiO_2, CaO and other mineralizers to lower the sintering temperature. These mineralizers react and form a glassy phase during sintering. The glassy phase between grains is believed to be the cause of the lower thermal conductivity of the commercial Al_2O_3 ceramics.

We sintered pure Al_2O_3 and Al_2O_3 with ZrO_2 as the second phase testing for a higher thermal conductive Al_2O_3 ceramic substrate(1,2). The measured thermal conductivity values ranged from 30 to 37 W/mK. These values were higher than those of commercial ceramic materials. However, the values do not coincide with those predicted from the models.

In this paper, we discuss the inconsistency of the measured values with those calculated from the models.

MATERIALS AND METHOD FOR THE DETERMINATION OF THERMAL CONDUCTIVITY OF PURE Al_2O_3 CERAMIC AND Al_2O_3/ZrO_2 COMPOSITES

High purity Al_2O_3 powders, AES11 and AKP30 (Sumitomo Chemicals Co., Ltd.), with and without ZrO_2 as grain growth inhibitor, were sintered to almost full density at a temperature range from 1550 to 1650°C in an electric furnace. AKP-30 was also sintered in a gas furnace at 1450-1550°C. The thermal conductivities were measured using a laser flash type instrument model TC-7000 ULVAC-RICO, at ULVAC-RICO Inc. Japan and Tokyo Institute of Technology (TIT). The size of the specimens were 10±0.5 mm in diameter and about 1.5 mm in thickness. The experimental details and original data are reported in references 1 and 2 which are MS theses at Chulalongkorn University. All thermal conductivity data are listed in the Appendix and properties of the Al_2O_3 powders are given in Table1.

The morphologies of Al_2O_3 with 0.5wt% of MgO, and with 7.5wt% of ZrO_2 are shown in Figures 1(A) and (B). Some of the grains of Al_2O_3 in the ceramic with 0.5wt% of MgO grew over 5μm as shown in photo (A). Grain boundaries were flat and it seems that there was no secondary phase. Zirconia (white particle) was in the grain boundary especially at the triple point between grains. See photo (B).

MODELS TO PREDICT THE THERMAL CONDUCTIVITY OF COMPOSITES

The thermal conductivity of a composite is affected by the morphology as well as the amount of the second phase. Very simple models are series slabs and parallel slabs. Series slabs models are composed of two phases perpendicular to the direction of heat flow while parallel slab models are parallel.

The thermal conductivity of a parallel model is simply expressed as in equation (1).

$$\kappa_m = v_1\kappa_1 + v_2\kappa_2 \qquad \ldots (1)$$

and that of a series model is as in equation (2).

$$\frac{1}{\kappa_m} = \frac{v_1}{\kappa_1} + \frac{v_2}{\kappa_2} \qquad \ldots (2)$$

κ_m is the thermal conductivity of a composite, κ_1, κ_2 and v_1, v_2 are the thermal conductivities and the volume fractions of phases 1 and 2 of the composite, respectively. In the parallel model, the heat conduction is contributed by the 2 phases but in the series model, it is dominated by the lower conductive phase. However these models do not coincide with the morphology of the specimens shown in Figures 1(A) and (B). The morphology shown in Figure 2 suggests a model with a continuous major phase (Al_2O_3 particles) with a minor amount of a discontinuous second phase (pore and ZrO_2 particles). The analytical model of the thermal conductivity of a composite with this morphology was proposed by Eucken(3,4) and it is shown in equation (3).

$$\kappa_m = \kappa_c \frac{1 + 2\nu_d (1 - \kappa_c / \kappa_d)/(2\kappa_c / \kappa_d + 1)}{1 - \nu_d (1 - \kappa_c / \kappa_d)/(2\kappa_c / \kappa_d + 1)} \qquad \ldots (3)$$

κ_c and κ_d are the thermal conductivities of a continuous phase and a discontinuous phase, respectively, and ν_d is the volume fraction of the discontinuous phase.

In this experiment, the continuous phase is Al_2O_3 and the discontinuous phases are ZrO_2 and pore. The thermal conductivities of Al_2O_3, ZrO_2 and pore are about 40W/mK, 3W/mK and nearly zero, respectively. To confirm the effect of the thermal conductivity of the discontinuous phase, the κ_m in equation (1), (2) and (3) was calculated for both cases, using either $\kappa_2 = \kappa_d = 3$ or zero. When $\kappa_d = 3$ or $\kappa_d = 0$, equation (3) is written as equation (4) or (5), respectively.

$$\kappa_m = 40\left[\frac{1 - 0.89\nu_d}{1 + 0.45\nu_d}\right] \qquad \ldots (4)$$

$$\kappa_m = 40\left[\frac{1 - \nu_d}{1 + \nu_d / 2}\right] \qquad \ldots (5)$$

In equation (2), the case of $\kappa_d = 0$ has no meaning. Calculated results are shown in Figures 3 and 4. As seen in Figure 3, the calculated value of thermal conductivity for the series slabs model is very much different from the other models. As seen in Figure 4, the calculated values from equation (2) are larger than those of equations (4) and (5). The calculated values for equations (4) and (5) are nearly the same in the two cases whether the lower thermal conductive phase is regarded as ZrO_2 or pore.

RESULTS AND DISCUSSIONS

The measured thermal conductivity data are plotted in Figure 5 as a function of percentage volume of Al_2O_3. As seen in Figure 5, the measured data are quite lower than those of the calculated values, therefore the calculated values of pore by equation (4) are used for discussion hereafter. The measured value was about 4 W/mK lower than the calculated value on average.

In the calculation, 40W/mK was used as the thermal conductivity of 100% Al_2O_3 ceramics because the ultimate high thermal conductivity of Al_2O_3 ceramics will be similar to that of a single crystal.(5) The thermal conductivity of sapphire, which is single-crystal of aluminum oxide, is 35-40 W/mK. Other data from websites show a high value of 46 W/mK and a low value of 27 W/mK.(6) KYOCERA produced a single-crystal of Al_2O_3 by EFG (Edge-defined Film-fed Growth) method.(7) The catalogue reported the thermal conductivity of the single-crystal of sapphire to be 42 W/mK. Moreover, it is known that the thermal conductivity of single-crystal Al_2O_3 varies with the crystal direction(6,8) because the crystal structure of Al_2O_3 is hexagonal. So far, we could not find any definite data on the thermal conductivity of Al_2O_3 ceramics. However, considering all the data mentioned above extrapolating the value of the measured maximum data in Figure 5, 40 W/mK as the thermal conductivity of 100% pure Al_2O_3 ceramics would be reasonable.

There was about 5W/mK deviation in the measured thermal conductivity for the same volume of Al_2O_3 as seen in Figure 5. One of the causes of the deviation may come from the difference in the shape of pores. When the shape of the pore is not round, i.e. thin gap, the detrimental effect of the pore on the thermal conductivity is greater. Besides round pores, there are some long and narrow pores shown by the arrow in Figure 1. It is difficult to analyze the shape of pores quantitatively, but it must be one of the causes of the deviation of the measured thermal conductivity.

Ceramics usually include some amount of grain boundary phase even it is sintered by the solid phase sintering mechanism.(9) The grain boundary phase will be a thin layer of distorted lattice or an impurity concentrated phase or a glassy phase. Although such grain boundary phase is not seen in Figure 2, it would be another detrimental factor of thermal conductivity. Figure 6 shows a similar graph as Figure 5, but the data are arranged into three groups. Round symbol (•) shows the data of specimens sintered at high temperature, 1600 and 1650°C, using AKP-30 powder. Square symbol (□) shows the data sintered at temperatures lower than 1550°C for the same AKP-30 powder. Delta symbol (△) shows the data for AES-11 powder specimens sintered at high temperature, 1600 and 1650°C.

Comparing the data of the same sintering temperature range, (•) and (□), the thermal conductivity of the specimens from AKP-30, is a little larger than those of AES-11 for the same volume of Al_2O_3. The data of raw powders, AES-11 and AKP-30, are shown in Table 1. There are not large differences in chemical purity in these two powders, *i.e.* the amount of impurity in AES-11 is about 0.2 wt%, and 0.01wt% in AKP-30. However, the impurity difference must cause the difference of grain boundary phase and result in the thermal conductivity difference. Considering only the specimens sintered at higher temperature and made from AKP-30 powder, the inconsistency between the calculated value and measured value decreased to about 2W/mK. The number of measurements is not enough to discuss statistically at this time, but this is an area of possible future study.

Comparing the data of the different sintering temperature ranges, the thermal conductivity of the specimens sintered at higher temperatures is a little larger than that of those at lower temperatures. The grain sizes of the specimens sintered at 1500-1550°C were 0.4-0.5µm and those at 1600-1650°C were 0.5-1.2 µm, respectively [10]. Smaller grain size means more grain boundaries. Therefore, the difference of the thermal conductivity of the two groups may be caused by the difference in the extent of grain boundaries too. Figure 7 shows the data for same specimens measured at two institutes. There is 2.2 W/mK difference on average. The room temperature during measurement in the two laboratories was 30-31°C and 18-22°C, respectively. The temperature coefficient of thermal conductivity of Al_2O_3 was reported to be about 0.07 W/mK.[6] Therefore, the contribution of the room temperature difference in the above two laboratories is about 0.7W/mK. Thus, there is 1.5 W/mK difference on average between the two institutes. So far the cause of the difference is not clearly known.

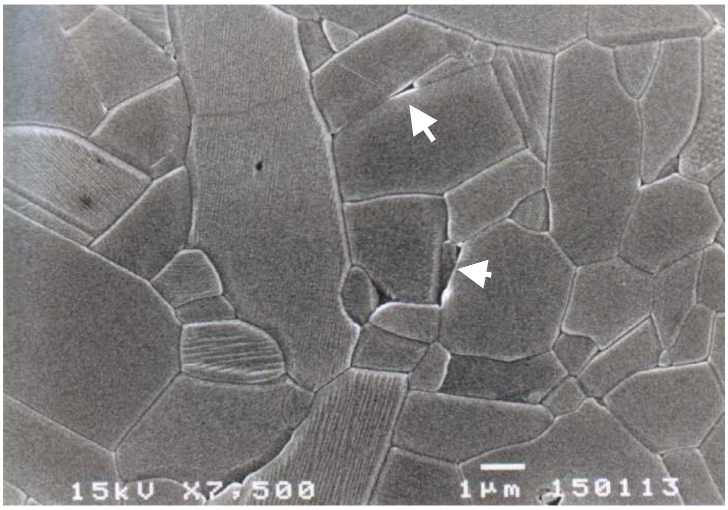
CONCLUSIONS

The thermal conductivity of high purity Al_2O_3 ceramic and Al_2O_3 ceramics with ZrO_2 as the second phase were measured by the Laser Flash Method. The measured thermal conductivity was analyzed by the Eucken model for a composite. However, the measured values were 4W/mK lower on average than those of the calculated values from this model. Also, there was about 5W/mK deviation in the measured value. The inconsistency between calculated values based on the models and measured values was thought to be caused by the difference in the shape of pores. Although the grain boundary second phase was not observed in the SEM micrographs, a small amount of the grain boundary phase must decrease the thermal conductivity of specimens and it was thought to be another cause of the inconsistency and deviation. A 1.5 W/mK difference was observed in the measurement by the two institutes.

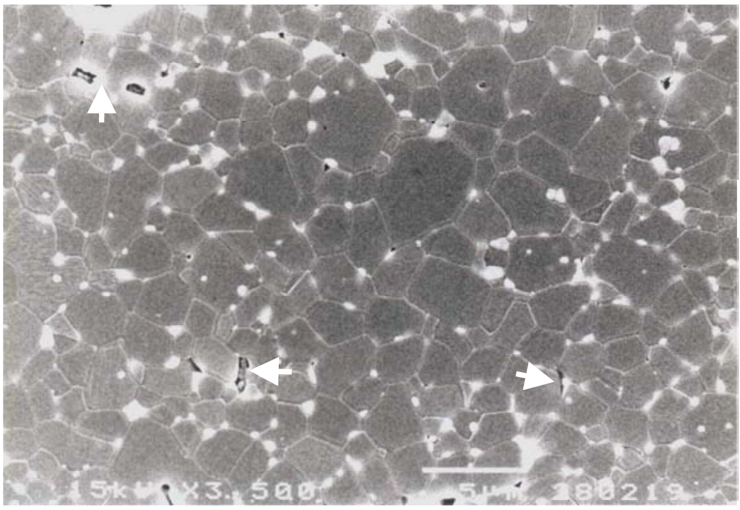
Table 1. Some properties of two raw powders, AKP-30 and AES-11.

Grade name		AKP-30	AES-11
Chemical Composition#	Al_2O_3 content (%)	>99.99	99.8
	L.O.I. (%)	-	0.1
	Na (ppm) /Na_2O (%)	≤ 10	0.04
	Fe (ppm) /Fe_2O_3 (%)	≤ 20	0.02
	Si (ppm) /SiO_2 (%)	≤ 40	0.06
	Mg (ppm)	≤ 10	0.1
	Cu (ppm)	≤ 10	-
Average grain size (µm)		0.3~0.5	0.5
Specific surface area (m^2/g)		5~10	-
Bulk density (g/cm^3)		0.7~1.0	-

#: The dimensions of impurities are ppm for AKP-30 and % for AES-11
L.O.I. = Loss on ignition



(A) AES-11 with MgO 0.5wt% sintered at 1650°C for 2h



(B) AKP-30 with ZrO_2 7.5wt% sintered at 1650°C for 2h

Figure 1. Morphologies observed by SEM of AES-11 with MgO 0.5wt% and AKP-30 with ZrO_2 7.5wt% sintered at 1650°C for 2h.

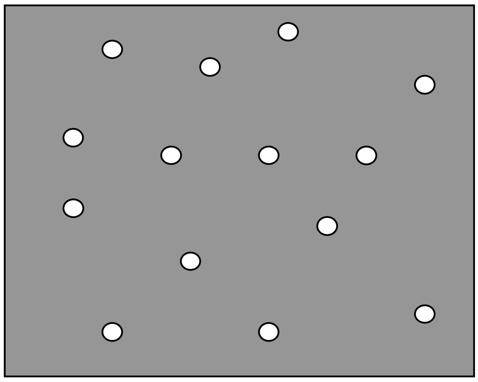


Figure 2. Model of a continuous major phase with a minor amount of a discontinuous second phase.

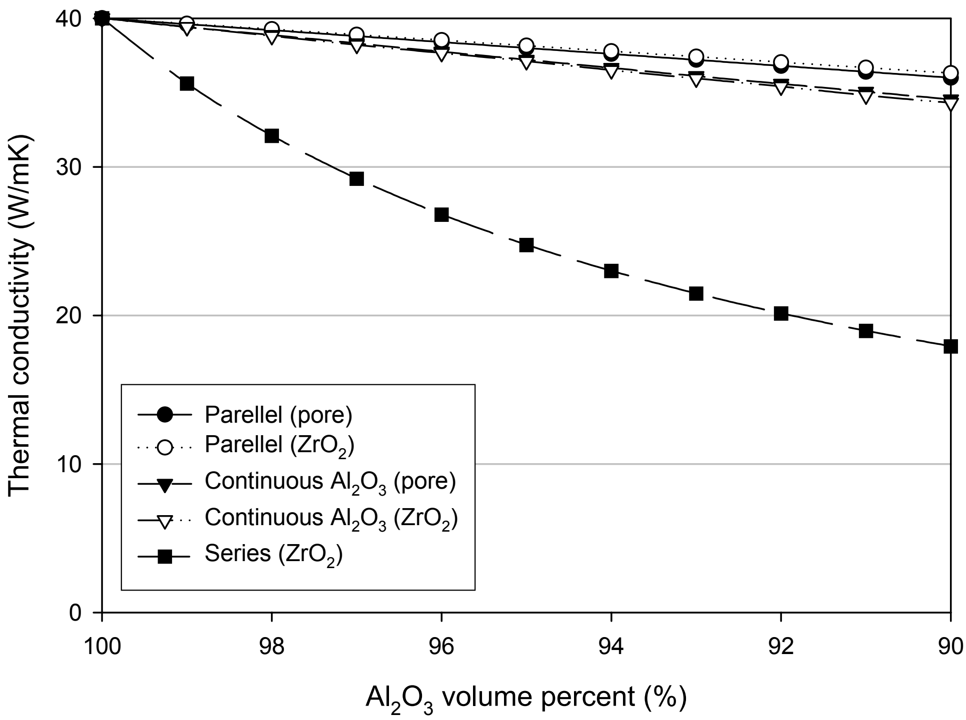


Figure 3. Calculated thermal conductivity values from several models.

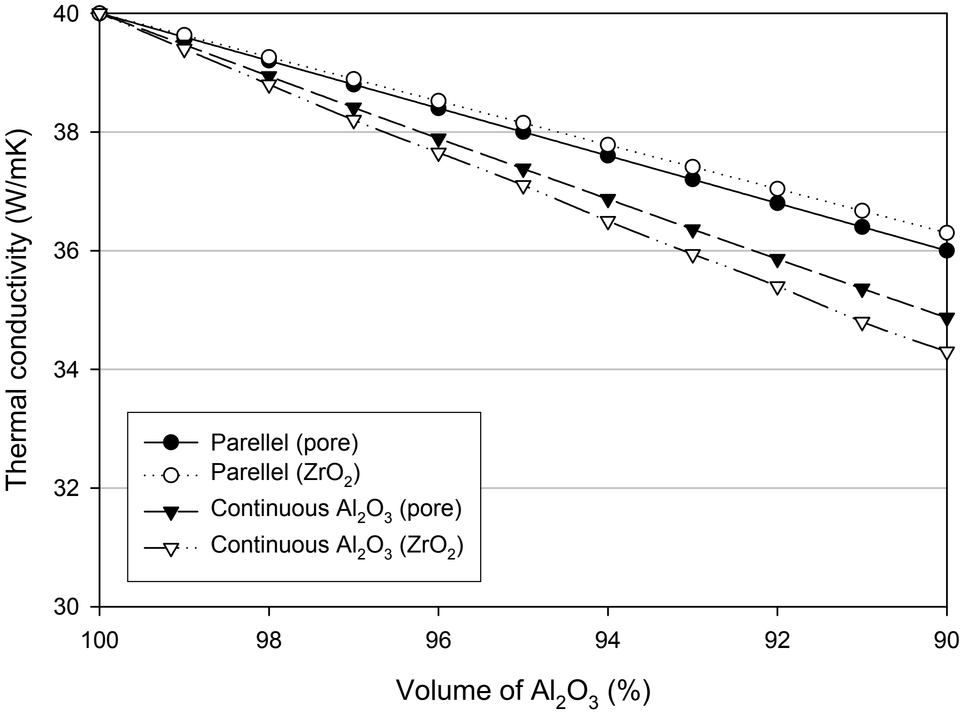


Figure 4. Calculated thermal conductivity for parallel and continuous Al_2O_3 models.

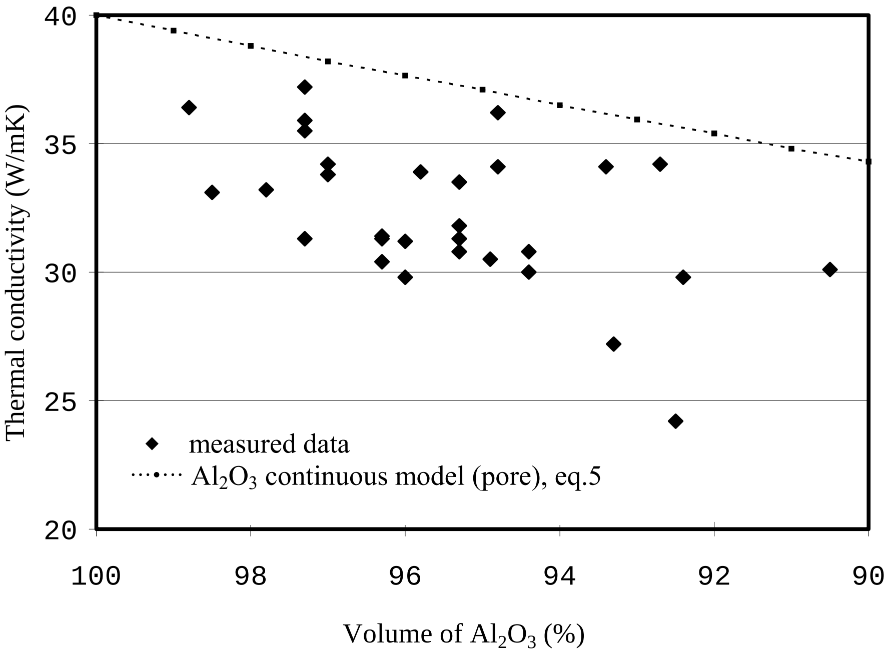


Figure 5. Relationship between volume of Al_2O_3 and thermal conductivity.

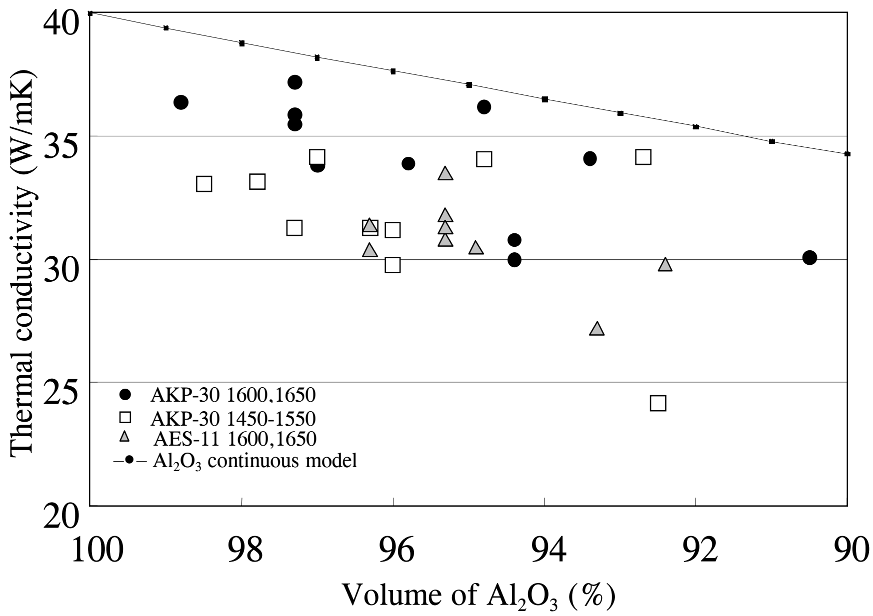


Figure 6. Thermal conductivity of Al_2O_3 as a function of raw powder and sintering temperature.

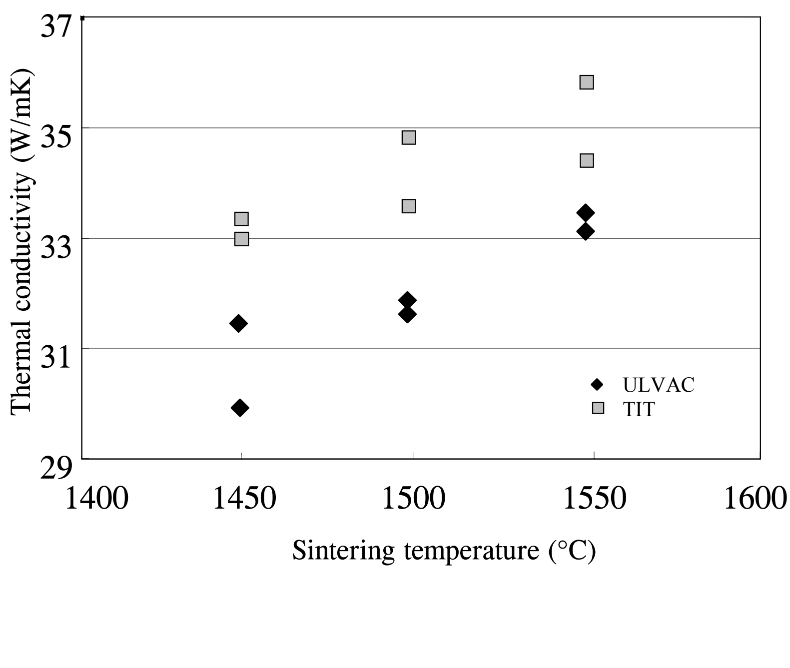


Figure 7. Relationship between thermal conductivity and temperature measured by the two institutes.

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APPENDIX

The thermal conductivity data are shown in Tables A-1 and A-2.
Relative density and porosities are calculated as follows:
True density is calculated from the weight ratio of components using the value of Al_2O_3: 4.00 g/cm^3, MgO: 3.64 g/cm^3 and ZrO_2: 6.02 g/cm^3. True densities calculated from this assumption are 4.00, 4.02, 4.04 and 4.10 g/cm^3 for the compositions with MgO 0.5 wt%, ZrO_2 1.5, 3.0 and 7.5 wt%, respectively.
*1 Relative density (Rd) = Bulk density (Bd) / True density (Td)
*2 Volume fraction of ZrO_2 (ν_z) = Rd (wt fraction of ZrO_2/1.5)
*3 Volume fraction of pore (ν_p) = 1-Rd
*4 Total porosity (Tp) = $\nu_z + \nu_p$
*5 Volume of Al_2O_3 (Va) = 1-ν_d

Table A-1 Experimental results of thermal conductivity (1)

Powder	Additives (wt%)	Sintering temp. (°C)	B_d (g/cm^3)	Rd*1	ν_z *2	ν_p *3	Tp*4	Va*5	Thermal Conductivity (W/mK)
AKP-30	-	1650	3.89	.973	0	.027	.027	.973	35.5
	MgO 0.5		3.89	.973	0	.027	.027	.973	37.2
	ZrO_2 1.5		3.79	.943	.0094	.057	.066	.934	34.1
	3.0		3.89	.963	.0193	.037	.056	.944	30.8
	7.5		3.91	.954	.0477	.047	.095	.905	30.1
AES-11	-	1650	3.81	.953	0	.047	.047	.953	31.8
	MgO 0.5		3.81	.953	0	.047	.047	.953	30.8
	ZrO_2 1.5		3.91	.973	.0097	.027	.037	.963	31.4
	3.0		3.93	.973	.0195	.027	.047	.953	33.5
	7.5		3.99	.973	.0487	.027	.076	.924	29.8
AES-11	-	1600	3.73	.933	0	.067	.067	.933	27.2
	MgO 0.5		3.85	.963	0	.037	.037	.963	30.4
	ZrO_2 1.5		3.87	.963	.0096	.037	.047	.953	31.3
	3.0		3.91	.968	.0194	.032	.051	.949	30.5

Table A-2 Experimental results of thermal conductivity (2)

Powder	Additives (wt%)	Sintering temp. (°C)	B_d (g/cm^3)	Rd*[1]	Vz*[2]	Vp*[3]	Tp*[4]	Va*[5]	Thermal Conductivity (W/mK)
AKP-30	-	1450	3.84	.960	0	.040	.040	.960	31.2
			3.84	.960	0	.040	.040	.960	29.8
		1500	3.89	.973	0	.027	.027	.973	31.3
			3.86	.965	0	.035	.035	.965	31.3
		1550	3.94	.985	0	.015	.015	.985	33.1
			3.91	.978	0	.022	.022	.978	33.2
AKP-30	MgO 0.5	1500	3.70	.925	0	.075	.075	.925	24.2
		1550	3.88	.970	0	.030	.030	.970	34.2
		1600	3.89	.973	0	.027	.027	.973	35.9
		1650	3.95	.988	0	.012	.012	.988	36.4
AKP-30	ZrO_2 1.5	1550	3.87	.963	.0096	.037	.0466	.953	34.1
		1600	3.85	.958	.0096	.042	.0516	.948	36.2
		1650	3.94	.980	.0098	.020	.0298	.970	33.8
AKP-30	ZrO_2 3.0	1550	3.82	.946	.0189	.054	.0729	.927	34.2
		1600	3.89	.963	.0193	.037	.0563	.944	30.0
		1650	3.95	.978	.0196	.022	.0416	.958	33.9

REFERENCES

1. Piempermpoon B.(2002) Improvement of Thermal Conductivity of Alumina for Peltier Element, MS thesis, Department of Material Science, Faculty of Science, Chulalongkorn University, ISBN 974-17-0850-5.
2. Na Nakorn P. (2003) Development of Alumina Substrate for Peltier Element, MS thesis, Department of Material Science, Faculty of Science, Chulalongkorn University, ISBN 974-17-4458-7.
3. Francl J. and Kingery W. D. (1954) "Thermal Conductivity: IX, Experimental Investigation of Effect of Porosity on Thermal Conductivity" *J. American Ceramic Society,* **37(2)** pp. 99-107.
4. Lawrence, H. and Van Vlack (1964) "Physical Ceramics for Engineers" 1st edition, pp. 147-155.
5. 35-40 http://www.azom.com/details.asp?ArticleID=1721%20
   40 http://global.kyocera.com/prdct/fc/product/pdf/s_c_sapphire.pdf
   35.1http://www.newrise-llc.com/sapphire.html
   34.9 http://www.reade.com/Particle_Briefings/thermal_con_ceramics.html
   40 http://www.industrialjewel.com/material.htm
6. 46 http://www.allceramic.com/sapphire.htm 27.3 // and 23.1┴ to c-axis http://www/jpmahk.com/izumi/izumi_hp3.html
7. KYOCERA catalogue 005/001/9911 017668 (1999)
8. 35 // and 32┴ to c-axis http://www.rfcafe.com/references/general/thermal_conductivity.htm
9. ibid with (3), (1976) pp.200-204.
10. Na Nakon, P., Jinawath, S. and Wada, S. (2005) "Mechanical Strength and Thermal Conductivity of High Purity Al_2O_3 Ceramics using AKP-30 Powder" *J. Sci. Res. Chula. Univ.,* **30(1)** pp. 77-85.

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