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Thermal Conductivity of Polymethyl Methacrylate (PMMA) and Borosilicate Crown Glass BK7

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The thermal conductivity of polymethyl methacrylate (PMMA) and borosilicate crown glass BK7 has been studied. The transient hot-wire technique has been employed, and measurements cover a temperature range from room temperature up to 350 K for PMMA and up to 500 K for BK7. The technique is applied here in a novel way that minimizes all remaining thermal-contact resistances. This allows the apparatus to operate in an absolute way and with very low uncertainty. The method makes use of a soft silicone paste material between the hot wires and the solid under test. Measurements of the transient temperature rise of the wires in response to an electrical heating step over a period of 20 μs up to 5 s allow an absolute determination of the thermal conductivity of the solid, as well as of the silicone paste. The method is based on a full theoretical model with equations solved by a two-dimensional finite-element method applied to the exact geometry. At the 95% confidence level, the standard deviations of the thermal conductivity measurements are 0.09% for PMMA and 0.16% for BK7, whereas the standard uncertainty of the technique is less than 1.5%.

KEY WORDS: BK7; borosilicate crown glass; PMMA; polymethyl methacrylate; thermal conductivity; transient hot wire.

1. INTRODUCTION

In a series of recent papers [1–4], a novel application of the transient hot-wire technique for thermal conductivity measurements on solids was described. One of the main advantages of this technique was the introduction of a soft-paste material between the hot wires of the technique and the solid under test, resulting in the minimization of wire-solid thermal-contact

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resistances and the absence of any air gaps. Thus, based on a full theoretical model with equations solved by a finite-element method applied to the exact geometry, it allows the accurate and absolute determination of the thermal conductivity of the solid. With this method, the thermal conductivity of a series of solids was successfully measured (Pyroceram 9606 up to 590 K [1, 2], AISI 304 L up to 550 K [3], and Pyrex 7740 up to 530 K [4]). These solid materials were of particular interest, as they cover a thermal conductivity range from about 1 to $14\,\mathrm{W \cdot m^{-1} \cdot K^{-1}}$ at 298 K. At the 95% confidence level, the standard deviations of the thermal conductivity measurements of Pyroceram 9606, AISI 304L, and Pyrex 7740 were 0.42, 0.20, and 0.13%, respectively, and of the volumetric specific heat capacity, ρC_p, 0.80, 0.16, and 0.10%, respectively. The standard uncertainty [5] of the technique is better than 1.5% for the measurement of the thermal conductivity and better than 5% for the measurement of the volumetric specific heat capacity.

In this paper the thermal conductivity of polymethyl methacrylate (PMMA) and of borosilicate crown glass BK7, will be examined. PMMA is an amorphous, colorless thermoplastic material of excellent optical transparency and a luminous transmittance of about 92%. It has good abrasion resistance and dimensional stability but is brittle and notch sensitive. Its water absorptivity is very low in comparison with other polymer materials. BK7 is widely used for optical systems and can be manufactured with outstanding homogeneity. It has isotropic thermophysical properties with excellent long-term stability.

PMMA was proposed by NPL as a possible candidate for a thermal conductivity reference standard in 2003 [6]. However, a more recent intercomparison between 17 laboratories, organized by Physikalisch-Technische Bundesanstalt (PTB) [7], showed uncertainties in the thermal conductivity values between 8 and 13%, which far exceeded the laboratories' quoted uncertainties. Hence, the employment of PMMA as an acceptable thermal conductivity standard is still under consideration.

In the case of BK7, a similar intercomparison among eleven European laboratories, also organized by PTB [8], aiming to qualify it as a possible candidate reference material for thermal conductivity, produced uncertainties up to 40%, which were far in excess of the laboratories' quoted uncertainties. Hence, this material is also still under consideration.

2. EXPERIMENTAL

The actual instrument employed for the measurement of the thermal conductivity of solids at elevated temperatures is described elsewhere [1] and will only be presented briefly here. In the case of PMMA and BK7, the same two-wire sensor [2] was employed.

The two wires, made of 25-μm-diameter tantalum wire of 2 and 5 cm lengths, placed one after the other, are spot-welded to flattened 0.5 mm diameter tantalum wires. These, in turn, are spot-welded to thick metal-sheathed Chromel wires, as shown in Fig. 1. The wires are subsequently placed in a flattened silicone paste layer (high-temperature red silicone paste, BORO 650, VersaChem, U.S.A.). The advantages of employing a soft silicone layer were discussed in previous publications [1, 2]. Finally, the two wires embedded in the silicone paste are sandwiched between two 25-μm-thick polyimide films (Kapton HN polyimide film, Du Pont de Nemours), and the whole assembly is then placed between two pieces of the solid of dimensions $10 \times 5 \times 2\,\text{cm}^3$, each. The polyimide film's great adhesive power to the glass produced a sensor that had no air gaps in its interface with the solid, while at the same time the sensor can easily be removed and reused. The full set of equations that needs, therefore, to be solved, refers to the heat transfer (a) in the wire, (b) in the silicone paste, (c) in the polyimide film, and (d) in the solid, with equivalent initial and boundary conditions. This set, as described above [3], was solved by a finite-element method for the exact geometry of the sensor.

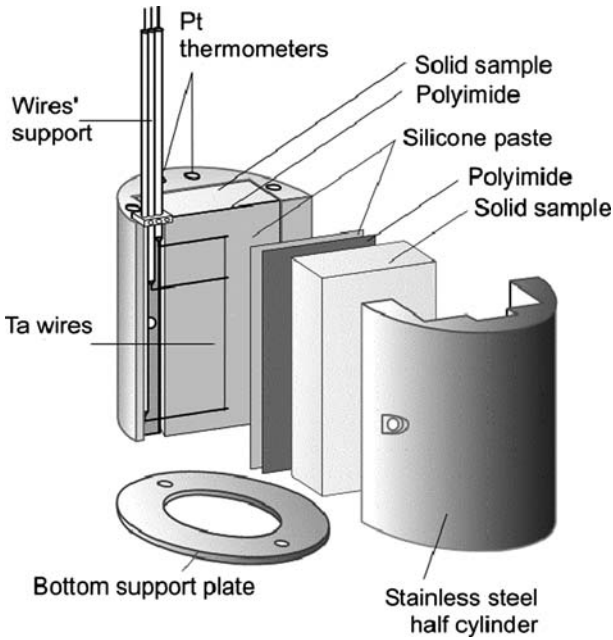

Fig. 1. Wire sensor arrangement.

The wire-sensor arrangement with the two solid blocks is held together in two semi-cylindrical parts made of AISI 310 steel (see Fig. 1). Consequently, the whole arrangement is placed in the center of a vertical three-zone tubular furnace (Model TVS 12, Carbolite), and two Class-1 calibrated platinum-resistance thermometers embedded on the top and bottom of one of the half cylinders, are used to record the temperature.

The wires are heated over a period of 5 s by electrical current, and the thermal conductivity is determined in an absolute way from the transient temperature rise of the wire. In order to heat the wires and measure their resistance at the same time, a computer-controlled Wheatstone bridge is employed [1]. As already discussed, the novelty of this technique is that the whole temporal temperature rise curve is used; see Fig. 2. Hence, the characteristics of the silicone-paste intermediate layer and the polyimide film are evaluated from measurements at short times (typically: $t < 0.4$ s for the silicone paste and $0.4 < t < 0.8$ s for the polyimide), whereas those of the solid are consequently derived essentially independently from measurements at longer times (typically: $t > 0.8$ s). Hence, the thermal conductivity, λ, and the volumetric specific heat capacity, (ρC_p), of the solid and the intermediate layers as well as the thickness of the silicone layer are uniquely determined from a thousand measurements of the temperature rise accumulated during one run. Temperature rises employed are between 3 and 4 K over a maximum period of about 5 s.

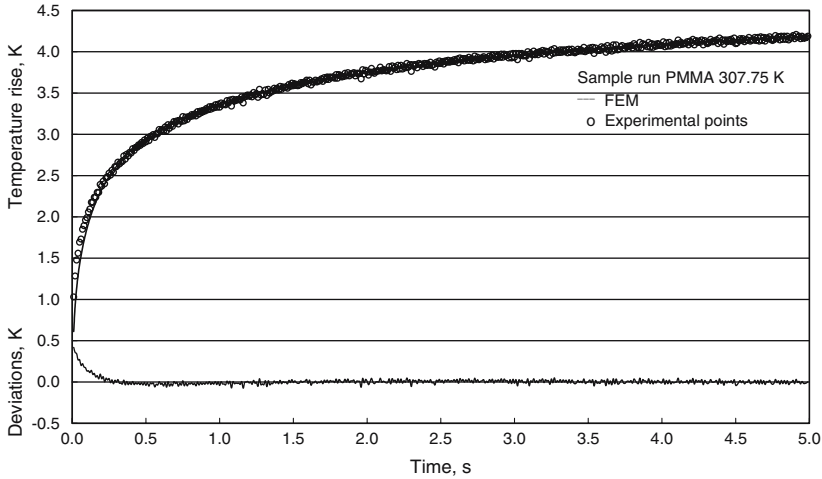

Fig. 2. Temporal temperature rise during a sample run on PMMA at 307.75 K.

3. MEASUREMENTS

3.1. Validation of Technique

The standard uncertainty of the measurement of the resistance of the wires is a function of the uncertainties of the time intervals and the associated applied voltage [1]. Time intervals are measured with a precision of ± 1 μs, whereas voltages are registered with a precision of 1 μV. The final result is also influenced by the standard uncertainty of the platinum-resistance thermometers. These have been calibrated with a standard uncertainty of ± 20 mK (ITS 90 temperature scale was employed). Accounting for a number of other small errors, such as the measurements of the wire lengths and the temperature coefficient of resistance of tantalum as well as errors associated with the finite-element analysis employed, it is estimated that the technique has a standard uncertainty of better than 1.5% in the measurement of the thermal conductivity, and better than 5% in the measurement of the volumetric specific heat capacity.

An important advantage of the proposed configuration is that it can also be employed to measure the thermal conductivity of fluids. So, the wires in their support, before being placed in the silicone layer, were placed in toluene at 295.15 K, and the thermal conductivity, λ, and the volumetric specific heat capacity, (ρC_p), obtained were in excellent agreement with literature values. Liquid toluene has been proposed by the Subcommittee on Transport Properties of the International Union of Pure and Applied Chemistry as a thermal-conductivity standard with an uncertainty of 0.5% [9].

3.2. Results and Discussion

The PMMA investigated in this work, produced by casting, was supplied by Degussa Röhm Plexiglas GmbH, and was made available to our laboratory by PTB. Its density was determined by weighing to be $1200\,\mathrm{kg \cdot m^{-3}}$ at 293.15 K. Further properties of this specific material can be found in the literature [7]. The BK7 employed in this work was manufactured and supplied by Schott AG, and was made available to our laboratory by PTB. Its density was determined by weighing to be $2504\,\mathrm{kg \cdot m^{-3}}$ at 293.15 K. Further properties of this specific material can also be found in the literature [8].

Our results for the thermal conductivity, λ, and the product (ρC_p) for PMMA and BK7 are shown in Table I. The thermal conductivity, λ $(\mathrm{W \cdot m^{-1} \cdot K^{-1}})$, values shown in Table I were fitted as a function of the absolute temperature T (K) with an equation,

Table I. Measured Properties of PMMA and BK7 as a Function of Temperature

T (K)	λ (W·m^{-1}·K^{-1})	$\Delta\lambda^a$ (%)	(ρC_p) (kJ·m^{-3}·K^{-1})	$\Delta(\rho C_p)^b$ (%)
Polymethyl Methacrylate (PMMA)				
307.75	0.1922	0.11	1677	0.52
316.97	0.1934	−0.22	1716	−0.33
326.53	0.1955	0.02	1764	−0.70
332.43	0.1966	0.13	1812	0.10
345.13	0.1979	−0.01	1896	0.71
352.65	0.1986	−0.02	1920	−0.30
Borosilicate Crown Glass BK7				
295.75	1.060	−0.03	1903	−0.90
326.62	1.085	−0.16	2017	1.03
350.06	1.105	0.36	2050	−0.16
375.43	1.115	0.11	2124	0.38
398.71	1.120	−0.47	2148	−1.17
424.98	1.140	−0.06	2247	0.38
448.91	1.160	0.04	2320	1.01
473.94	1.190	0.27	2369	0.43
497.72	1.220	−0.19	2392	−1.02

[a] $\Delta\lambda = 100 \times (\lambda_{exp} - \lambda_{fit})/\lambda_{fit}$

[b] $\Delta(\rho C_p) = 100 \times [(\rho C_p)_{exp} - (\rho C_p)_{fit}]/(\rho C_p)_{fit}$

$$\lambda = \lambda\,(298.15\,\mathrm{K}) \sum_i a_i \left(\frac{T}{298.15}\right)^i \tag{1}$$

where the coefficients a_i and the values of λ (298.15 K) are shown in Table II. The maximum deviations of the experimental points (presented in Table I) from the above equation are 0.22 and 0.47% for PMMA and BK7, respectively. At the 95% confidence level, the standard deviations of the thermal conductivity measurements of PMMA and BK7 are 0.09%, and 0.16%, respectively, which are well within the standard uncertainties of the technique.

The volumetric specific heat capacity values shown in Table I were also fitted as a function of the absolute temperature T (K) with an equation,

$$\rho\, C_p = (\rho\, C_p)(298.15\,\mathrm{K}) \sum_i b_i \left(\frac{T}{298.15}\right)^i, \tag{2}$$

where the coefficients b_i and the values of (ρC_p) (298.15 K) are shown in Table II.

Table II. Coefficients and Standard Deviations of Eqs. (1) and (2)

	PMMA	BK7
Eq. (1)		
λ (298.15 K) ($W \cdot m^{-1} \cdot K^{-1}$)	0.18987	1.0630
a_0 (−)	−0.02222	−0.55678
a_1 (−)	1.67196	3.53903
a_2 (−)	−0.64984	−2.69192
a_3 (−)	0	0.70946
σ(95% confidence level) (%)	0.09	0.16
Eq. (2)		
(ρC_p) (298.15 K) ($kJ \cdot m^{-3} \cdot K^{-1}$)	1614.1	1926.0
b_0 (−)	−0.05640	0.61922
b_1 (−)	1.05638	0.38080
σ(95% confidence level) (%)	0.39	0.45

The maximum deviations of the experimental points (presented in Table II) from the above equation are 0.71 and 1.17% for PMMA and BK7, respectively, whereas at the 95% confidence level, the standard deviations of the product (ρC_p) are 0.39 and 0.45%, respectively.

In Fig. 3, the percentage deviations of the thermal conductivity values of PMMA obtained in this work, from the values calculated by using Eq. (1), are shown as a function of the temperature. As already mentioned, Tye and Salmon [6] in 2003 proposed after a very careful investigation aiming to produce a candidate thermal conductivity reference polymer, an equation for the thermal conductivity of PMMA with an uncertainty of ±1% at the 95% confidence level. The deviations of this equation (also shown in Fig. 3) from values calculated by using Eq. (1) are in excellent agreement with the present measurements.

In 2004, Rudtsch and Hammerschmidt [7], also aiming to propose a thermal conductivity reference material candidate, coordinated at PTB an intercomparison project for PMMA involving 17 European laboratories. Unfortunately, the thermal conductivity values produced even at 30 °C ranged from 0.16 to 0.21 $W \cdot m^{-1} \cdot K^{-1}$. It was suspected that the probable reason for this discrepancy was the not-properly-treated effect of contact resistance. To independently prove that the thermal contact resistance was adequately taken into account, values obtained by PTB by two different methods (guarded hot plate, transient hot strip) were also reported in the same paper. The deviations of these values (shown in Fig. 3) from the values calculated by using Eq. (1) are well within the mutual uncertainty of the instruments.

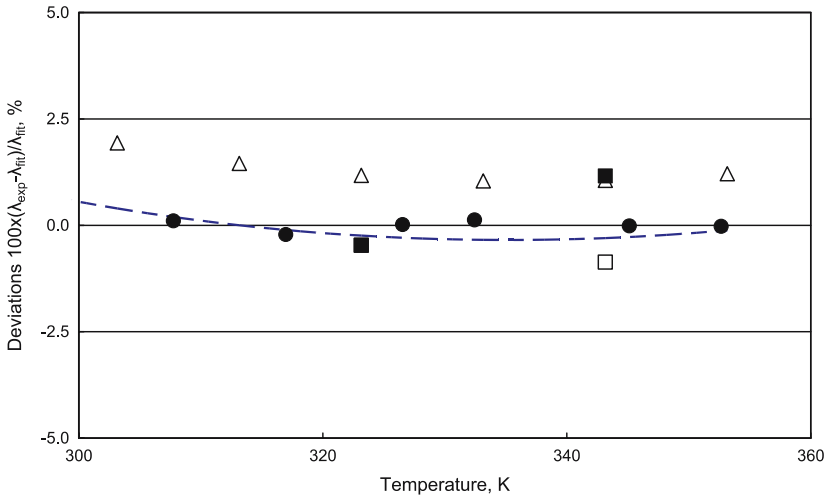

Fig. 3. Percentage deviations of the thermal conductivity measurements of PMMA as a function of temperature, from the values calculated by using Eq. (1). (●) Present work; (△) Rudtsch and Hammerschmidt [7]; (- - -) Tye and Salmon [6]; (□) guarded hot-plate data, (■) transient plane-source data, Boumaza and Redgrove [10].

There are a few other investigators who have measured the thermal conductivity of PMMA. We have chosen not to present here values from investigators who report only one measurement, and that at "room temperature," quoting no exact reference temperature and no uncertainty in their measurement. Boumaza and Redgrove [10] employed a transient plane-source (Gustaffson probe) and a guarded hot-plate instrument to investigate the thermal conductivity of PMMA with temperature. Their result, characterized by 5% reproducibility (shown in Fig. 3) agrees very well with the present measurements. We should finally mention the very interesting comparisons of various methods of measurements employed for the thermal conductivity of PMMA, carried out by Kubicar and Bohac [11] and Lockmuller et al. [12].

In the case of BK7, Rudtsch et al. [8], aiming to propose a thermal conductivity reference material candidate, also coordinated at PTB an intercomparison project for BK7 involving eleven laboratories. The results for thermal conductivity typically showed an 8% spread in the low temperature range, whereas at higher temperatures this rose to 40%. It was thus concluded that further investigation was necessary.

The only other data for the thermal conductivity of BK7 available, to our knowledge, are the measurements of Kubicar et al. [13] and of Ebert [14]. Kubicar et al. [13] employed a pulse transient method with a quoted

uncertainty of 5%. The deviation of his value (shown in Fig. 4) from that calculated by using Eq. (1), is well within the mutual uncertainties. Ebert [14] employed a double-plate instrument and a laser flash. No uncertainty was specified. His results for both methods (shown in Fig. 4) deviate up to 6% from the values calculated by using Eq. (1).

Figure 5 shows our measurements of the volumetric specific heat capacity for PMMA. In the same figure, the values reported by Rudtsch and Hammerschmidt [7] are also shown. The agreement is excellent. In Fig. 6, our measurements of the volumetric specific heat capacity for BK7 are shown. To our knowledge, no other set has been reported.

4. CONCLUSIONS

A recently developed transient hot-wire instrument for the measurement of thermal conductivity of solids was employed for the measurement of the thermal conductivity of polymethyl methacrylate PMMA and borosilicate crown glass BK7. The method, based on a full theoretical model with equations solved by finite elements for the exact geometry, allows absolute measurements with very low uncertainty. At the 95% confidence level, the standard deviations of the thermal conductivity measurements of PMMA and BK7 are 0.09 and 0.16%, respectively, and of the volumetric

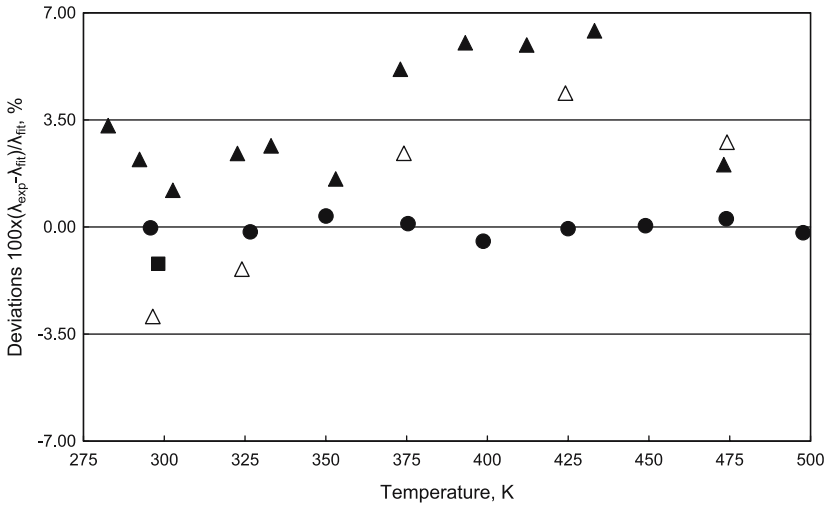

Fig. 4. Percentage deviations of the thermal conductivity measurements of BK7 as a function of temperature, from the values calculated by using Eq. (1). (●) Present work; (■) Kubicar et al. [14]; (△) laser-flash data, (▲) double- plate data, Ebert [13].

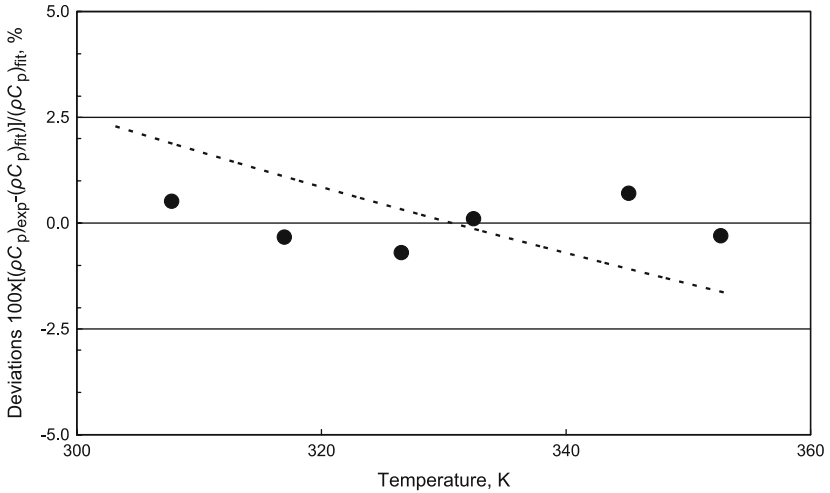

Fig. 5. Percentage deviations of volumetric specific heat capacity, (density × specific heat capacity), measurements of PMMA as a function of temperature, from the values calculated by using Eq. (2). (●) Present work; (- - -) Rudtsch and Hammerschmidt [7].

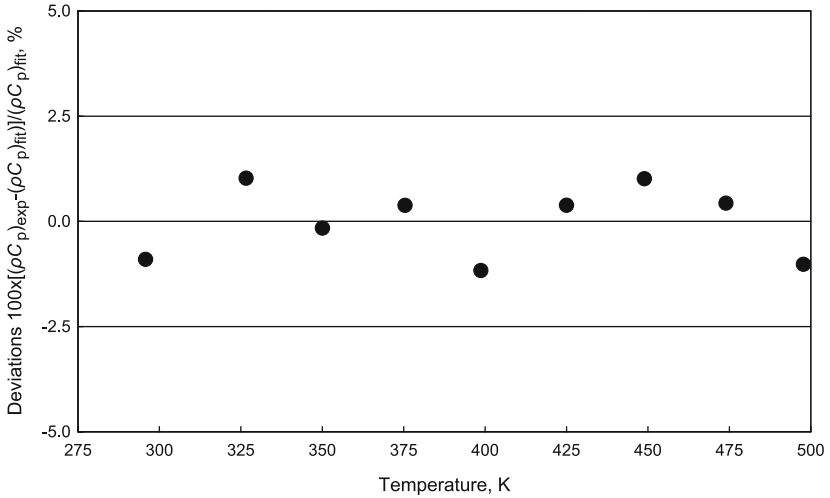

Fig. 6. Percentage deviations of volumetric specific heat capacity, (density × specific heat capacity), measurements of BK7 as a function of temperature, from the values calculated by using Eq. (2). (●) Present work.

specific heat capacity 0.39 and 0.45%, respectively. The technique has a standard uncertainty of better than 1.5% in the measurement of the thermal conductivity, and better than 5% in the measurement of the volumetric specific heat capacity.

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