

# Water-Glass-Based Thermal Paste for High-Temperature Applications

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## Abstract

Inorganic water-glass-based thermal pastes exhibit a higher thermal conductivity coefficient than silicon-based pastes. They can also be used at elevated temperatures. The optimum filler content, silicate modulus, application of a modifier and pressure were studied. As the result, a significant increase in the thermal conductivity at 508 °C could be explained. The MgO-Na<sub>2</sub>O-SiO<sub>2</sub> system with high magnesium oxide content has not been studied adequately, so special attention is paid to this system composition.

*Keywords:* Water glass, silicate modulus, magnesium oxide, boron nitride, thermal conductivity, porosity, thermal paste, composite material

## I. Introduction

In microelectronics and light engineering, key recent objectives have included achieving a significant improvement in energy efficiency. The application of LED engineering is the best option to achieve this objective, but this requires effective heat dissipation.

As installations become more powerful, they demand effective cooling systems. A big disadvantage of such systems is the application of silicon-based thermal pastes, the performance of which suffers severely after just a few months of operation<sup>1</sup>.

Thermal pastes are also required in special high-temperature fields. For instance, excellent thermal contact is required between the stainless steel heat pipe and carbon-carbon radiant plate refrigerator panel in thermo-emission nuclear installations. The main problem is the substantial difference in the CTE of the materials. Obviously, thermal pastes could be a suitable solution here<sup>2–3</sup>. However, the working temperatures in such an installation can achieve 600–800 °C, so evidently silicon matrixes cannot be used. High electrical conductance, corrosion activity and low oxidation resistance at such temperatures exclude the possibility of using liquid metal matrixes.

As a potential binder, water glass meets most requirements as it exhibits sufficient thermal conductivity (0.57 W/m × K, i.e. five times higher than silicon) as well as excellent corrosion and radiation resistance. Thanks to the low density of sodium water glass (about 1.42 g/sm<sup>3</sup>), the filling process is easier. The application of such a binder can be economically viable, which is another requirement. The filler was chosen based on several reasons, namely sufficient resistivity, thermal conductivity and corrosion (chemical) resistance to the selected binder. Whereas water glass contains up to 60 % water, the filler material must not react with it. It should also be mentioned that the filler

density is one of the most important factors, as the installation weight plays a significant role.

Based on the requirements and economic factors, magnesium oxide (MgO) of analytical grade was selected as filler.

## II. Experimental

The raw materials were weighed in Vibra HT-220CE analytical scales with an accuracy ± 0.0001 g, and ground in a porcelain pestle and mortar for 5–7 min. After that, a small portion of binder was weighed in a small crucible and the raw materials placed in this. The materials were mixed until a homogeneous paste-like consistency was obtained. The magnesium oxide to water glass ratio was within 1:2.5–1:3.5, which was determined empirically. Samples were obtained by filling the paste substance into cylindrical cells with a diameter of 12.7 mm and a depth of 4.5 mm, positioned in a flat and square Teflon mould.

The samples were left in the air environment and at room temperature until the first step of drying and solidification were completed. The two processes occur simultaneously, but the rate is different for various materials: from a couple of hours to a several days. The material can solidify or a half-hard tempered condition is sufficient for further transportation and processing.

The samples were then removed from the mould and dried by heating up to 120 °C in 2 h until evaporation of the volatile components was almost complete, shrinkage was complete and solidification was sufficiently complete in order to allow further heat treatment.

The following technological step was calcination of samples at the temperatures from 600–630 °C for 1 h. The choice of temperature was connected with the forced ageing and working temperatures of the product.

The samples were mechanically processed up to the dimensions required for analysis. The final samples with a

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weight of about 1 g in tablet form were analysed to determine the following properties:

- Bulk density ( $\text{g/cm}^3$ )

$$\rho = m/V \quad (1)$$

where  $m$  is the sample weight and  $V$  is the geometric volume;

- Water absorption in a vacuum (percent):

$$V = m_w \cdot 100 / m_s \quad (2)$$

where  $m_w$  is the weight of the absorbed water weight and  $m_s$  is the weight of the dried sample;

- Open porosity (percent):

$$P = m_w \cdot 100 / V \quad (3)$$

Thirteen samples of the thermally conductive composite material were prepared:

**Samples N 1–4:** Water glass (molar ratio  $\text{SiO}_2:\text{Na}_2\text{O} = 3:1$ ) composite materials were filled with MgO (filler content in the range of 25.0–36.5 vol%).

**Samples N 5–6:** The volume content was increased up to 50 % with the application of a boron nitride modifier. The following fillers ratios (BN/MgO) were prepared: 1:1 and 1.5:1.

**Sample N 7:** Water glass (molar ratio  $\text{SiO}_2:\text{Na}_2\text{O} = 3:1$ ) composite materials were filled with BN (35 vol%).

**Sample N 8:** Magnesium oxide mechanically activated for 12 h in a ball mill was mixed with a raw magnesium oxide in the ratio of 1:1. The filler content was 30 vol%.

**Samples N 10–13** Sodium water glass with molar ratio  $\text{SiO}_2:\text{Na}_2\text{O}$  in the range 2.0–4.0 was filled with magnesium oxide up to 30 vol%.

### III. Results and Discussion

#### (1) Water absorption analysis

The first samples (N 1–4) were analysed. The tablets were weighed and the dimensions measured with a thickness gauge with an accuracy  $\pm 0.01$  mm. The samples were placed in distilled water and evacuated in a VDO 3.5 “Templopribor” drying oven equipped with a 2NVR5DM pump (the ultimate residual pressure  $6.6 \cdot 10^{-4}$  Pa). After 15 min holding for maximum water absorption, the samples were weighed. Water absorption and porosity were calculated with formulae 2 and 3.

The porosity was in the range of 40–46 %. This rather high porosity is due to the high content of water in the binder, which evaporates to form pores. The pore dimensions depend on a variety of parameters, such as the dry-

ing temperature, the properties of the raw materials and the production technology.

#### (2) Thermal conductivity analysis

The thermal conductivity of the composite materials was determined with the laser flash approach in an Anter Flashline 4010. The Flashline System measures thermal diffusivity and determines thermal conductivity and specific heat capacity. The thermal conductivity  $\lambda$  is defined as  $\lambda = (Q/A)/(DT/DL)$ , where  $(Q/A)$  is the heat flux;  $Q$  is the amount of heat passing through a cross-section  $A$  of a sample;  $(DT/DL)$  is the resultant thermal gradient ( $DT$  temperature difference over  $DL$  length along the heat flow).

The specific heat capacity  $C_p$  of a material is the amount of heat required to raise the temperature of 1 g of material by 1 K. The specific heat can be measured with the laser flash method by comparing the increase in temperature of the sample with the increase in temperature of a reference sample of known specific heat tested under the same conditions<sup>5</sup>.

The thermal diffusivity  $\alpha$  of a medium is the thermophysical property that determines the speed of heat propagation by conduction during changes of temperature over time. The higher the thermal diffusivity, the faster the heat propagation. Thermal diffusivity is related to thermal conductivity  $\lambda$ , specific heat  $C_p$  and density  $\rho$  as follows:  $\alpha = \lambda / \rho \cdot C_p$ .

The standard configuration was used with a 200–300  $\mu\text{s}$  pulse width.

To study the thermal conductivity at elevated temperatures, the dependence of density on temperature must be known. CTE calculations were performed based on the Kengeri approach:

$$\rho(\text{theor}) = 2,429.05 \text{ g/sm}^3$$

$$\gamma(\text{theor}) = 7,594 \cdot 10^{-6} \text{ }^\circ\text{C}^{-1}.$$

The measurements were conducted at the room temperature. The test results are shown in Table 1.

**Table 1:** Test results of the dependence of thermal conductivity on the composition.

Sample	MgO [vol%]	Binder [vol%]	$\Lambda$ [W/(m·K)]
1	25	75	$1.71 \pm 0.08$
2	30	70	$1.73 \pm 0.08$
3	35	65	$1.81 \pm 0.09$
4	36.5	63.5	$1.8 \pm 0.09$

From analysis of the results, it is obvious that the highest thermal conductivity is achieved with MgO 35 vol%. A further increase in the filler content does not lead to the increase in the thermal conductivity coefficient owing to inevitable porosity of at least 30–40 %

Theoretically, the introduction of more heat-conducting material will increase the thermal conductivity of the system. Boron nitride was selected as a modifier on account of its excellent thermo-physical characteristics, name-

ly the thermal conductivity of boron nitride can reach  $180 \text{ W}/(\text{m}\cdot\text{K})$  <sup>7</sup>.

The measurement data are shown in Table 2.

**Table 2:** Dependence of the thermal conductance on the BN volume content.

No.	MgO [vol%]	BN, [vol%]	Binder [vol%]	$\lambda$ , [W/(m·K)]	Water absorption [%]	Porosity [%]
5	20.0	30.0	50.0	$1.63 \pm 0.08$	$17 \pm 1$	$36 \pm 3$
6	25.0	25.0	50.0	$1.52 \pm 0.07$	$19 \pm 1$	$41 \pm 3$
7	0.0	30.0	70.0	$0.57 \pm 0.03$	$30 \pm 2$	$70 \pm 5$

Owing to the application of the modifier, porosity decreased slightly, and a reduction in thermal conductance was also observed. Consequently, boron nitride was studied as the main filler. Samples prepared with the technology changed their colour directly in contact with the water glass. After calcination at the working temperatures, a glaze-like glassy gloss appeared. Considerable shrinkage and enormous porosity were also observed.

As the result it has been supposed, that during preparation of the composite material the boron nitride partially oxidized to amorphous boron oxide, which possessed a thermal conductivity coefficient of around  $0.51 \text{ W}/(\text{m}\cdot\text{K})$  <sup>8</sup>. It largely explains the high porosity caused by gas formation during oxidation and is perfectly consistent with the experimental data.

Based on test results it can be concluded that the porosity of the composite could be reduced with the application of the modifier. However, this must meet the following requirements: the modifier should not oxidize in contact with water, it should not sublimate at working temperatures, it should possess high thermal conductance coefficient value, low density and a low CTE.

The following part of the study refers to particle size reduction.

The raw magnesium oxide powder was ground in a ball mill for 12 h. The ground powder was mixed with a raw powder in the ratio 1:1. As a comparison, a sample containing only raw magnesium oxide was prepared.

**Table 3:** Dependence of the thermal conductivity on the silicate modulus of the binder.

Silicate modulus	$\lambda_{\text{binder}}$ [W/(m·K)]	$\lambda_{\text{exp}}$ [W/(m·K)]
2	$1.02 \pm 0.05$	$1.36 \pm 0.07$
2.2	$1.09 \pm 0.05$	$1.46 \pm 0.07$
2.5	$1.18 \pm 0.06$	$1.60 \pm 0.08$
2.7	$1.21 \pm 0.06$	$1.64 \pm 0.08$
3.0	$1.26 \pm 0.06$	$1.71 \pm 0.08$
4.0	$1.25 \pm 0.06$	$1.70 \pm 0.08$

The composite materials with activated MgO have a thermal conductivity coefficient  $\lambda = 2.1 \pm 0.1 \text{ W}/(\text{m}\cdot\text{K})$ . A sam-

ple with a similar volume filling with raw magnesium oxide has the value  $\lambda = 1.71 \pm 0.07 \text{ W}/(\text{m}\cdot\text{K})$ . Accordingly, the composite material filled with the more dispersed powder has a higher thermal conductivity value.

In the literature <sup>9</sup>, it has been suggested that the molar ratio  $\text{SiO}_2:\text{Na}_2\text{O}$ , the so-called silicate modulus, affects thermal conductivity.

The binder was modified by dissolving NaOH in it. A number of water glasses with a silicate modulus ranging from 2.0 to 4.0 were produced. Experimental data of the thermal conductivity measurement is shown in Table 3.

### (3) Dependence of thermal conductivity on temperature

Sample N2 was selected for study owing to its good thermal conductivity and satisfactory porosity. Measurements were conducted in the temperature range  $26 - 508^\circ\text{C}$ . The experimental data are shown in Table 4.

**Table 4:** Dependence of the thermal conductivity on temperature.

T [°C]	$\Lambda$ [BT/(M·K)]
26	$1.71 \pm 0.08$
192	$1.55 \pm 0.07$
358	$1.52 \pm 0.07$
508	$1.68 \pm 0.08$

The thermal conductivity clearly decreases with the increase in temperature, however, an increase in the thermal conductivity coefficient value is observed when the temperature reaches  $508^\circ\text{C}$ . This could be explained by the CTE of the material, the pores becoming smaller as the result after achieving a temperature threshold, the heat transfer area increasing significantly.

## IV. Conclusions

1. The application of water glass as a binder in composite materials leads to porosity of the samples, however, great adhesion and bonding of surfaces between which the thermal paste is applied provide a significant advantage over silicon-based pastes;
2. The environmental- and safety-related advantages of water glass compared to silicon make them more attractive for application;
3. The optimum magnesium oxide content is 35 vol%, which leads to a thermal conductivity coefficient of no less than  $1.73 \pm 0.08 \text{ W}/(\text{m}\cdot\text{K})$ , that is 70–90 percent higher than the value of similar silicon-based paste;
4. Use of more dispersed filler has a positive effect on the thermophysical properties of the samples;
5. The filler could be modified with a highly thermal-conductive compound with high oxidation resistance.
6. 2.9–3.2 was identified as the optimal sodium water glass silicate modulus;

7. Elevated temperatures significantly affect the thermal conductivity of the composite material owing to the reduction in pores;
8. The application of such paste in LED enables a significant system temperature decrease of about 5–7 K.

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