

Laboratorní a výpočetní technika

CaMgSi₂O₆ MELT, A STANDARD SUBSTANCE FOR CONDUCTIVITY MEASUREMENTS AT TEMPERATURES ABOVE 1500 K

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Over the temperature range of 1570 to 1880 K, the conductivity of the melt having the composition CaMgSi₂O₆ can be described by the equation

$$\log \frac{\kappa}{S \text{ cm}^{-1}} = 5.688 - 2.934 \times 10^4 T^{-1} + 5.678 \times 10^7 T^{-2} - 4.268 \times 10^{10} T^{-3}$$

while the standard deviation of the experimental values from the regressive equation $\sigma = 0.002$. The correctness of the experimental values was verified by the free volume theory, by comparing the experimentally established transformation temperature with the T_0 value computed on the basis of the free volume theory. In view of the satisfactory agreement of the values, the melt of CaMgSi₂O₆ can be recommended as a standard substance for conductivity measurements at temperatures above 1500 K.

INTRODUCTION

Measurement of electrical conductivity of oxidic melts at temperatures exceeding 1500 K is experimentally quite demanding and yields conductivity values mostly involving a considerable error. This is due to the principle of relative measurement by comparing the resistance values measured with the resistance of a standard substance, and to the way the conductivity cell is calibrated; the calibration has so far been carried out mostly at room temperature using suitable standard solutions of inorganic salts and the resistance capacity values of the conductivity cell have been calculated for the higher temperatures by means of thermal expansion data. With this calibration method one has obviously to take into account possible deformation of the conductivity cell resulting from the heating up. The results of the measurements obtained in this way are precise with respect to the mutual relations, but may involve a certain absolute error.

The unsuitable way of calibrating the conductivity cell is essentially caused by the fact that for temperatures above 1500 K there has not so far been any convenient standard substance whose conductivity could be determined with adequate accuracy and particularly correctness. Although there are some inorganic salts such as K₂SO₄ or Na₃AlF₆ whose melting point is around 1300 K and whose conductivity is known with adequate accuracy and correctness, their use as standards for high-temperature conductivity measurements is unsuitable owing to the relatively high pressure of their vapours and the associated contamination of the high-temperature part of the measuring apparatus which leads to its rapid deterioration. The capillary cell cannot be used at high temperatures owing to the non-availability of suitable materials.

The melt of diopside, $\text{CaMgSi}_2\text{O}_6$, was therefore suggested as a reference substance for conductivity measurements at temperatures above 1500 K as a result of the present study. The suitability of the compound is based on its satisfactory thermal stability at high temperatures, its easy preparation and a well defined melting point. Diopside was already used in studies [1, 2], just because of these properties, as a secondary standard in the calibration of thermocouples. The melt of $\text{CaMgSi}_2\text{O}_6$ can be kept undercooled by 100 K for periods of time adequate for calibration. The present study was therefore concerned with careful conductivity measurements on this melt by means of the conventional calibration procedure, and the correctness of the values measured was verified by means of the free volume theory, i.e. by comparing the experimental transformation temperature value with that calculated from the conductivity data.

EXPERIMENTAL

The electrical conductivity measurements were carried out by means of a conductivity cell consisting of two disk electrodes 5 mm in diameter fixed at a mutual distance of 15 mm and made of PtRh 20 alloy. The conductors, 1 mm in diameter, were of the same material. The resistance was measured with the TESLA BM-484 semiautomatic bridge with a built-in source of alternate current of 1592 Hz frequency and a zero indicator. The conductivity cell was calibrated at room temperature with aqueous solutions of KCl. For the high-temperature measurements, the resistance capacity of the conductivity cell was calculated by means of the thermal expansion data of the PtRh20 alloy. About 100 g of the $\text{CaMgSi}_2\text{O}_6$ melt was placed in a PtRh20 crucible at the centre of an electric resistance furnace. The conductivity measurements were carried out over the temperature range of 1570 to 1880 K. The sample temperature was measured by a PtRh6 — PtRh30 thermocouple whose hot joint was placed directly in the melt. The relative accuracy of the conductivity measurement was $\pm 2\%$, that of the temperature measurement was ± 3 K. A detailed description of the apparatus employed was presented in [3].

The sample was prepared by calcinating the corresponding amounts of CaCO_3 A.R. and MgCO_3 A.R. at 1300 K for 2 hours and subsequent melting with pre-annealed SiO_2 A.R. in a stoichiometric ratio. The glass samples for transformation temperature measurements were obtained by pouring a molten sample into a water-cooled platinum dish. Before the measurements the glass was annealed for 5 hours at 950 K. The transformation temperature was determined by DTA and expansion measurements in three different laboratories.

RESULTS AND DISCUSSION

The values of conductivity of the $\text{CaMgSi}_2\text{O}_6$ melt measured over the temperature range of 1570 to 1880 K are listed in Table I. The values specified for the individual temperatures are means of 3 to 5 measurements. The least squares method was used to derive the following equation for the temperature dependence of conductivity

$$\log \frac{\kappa}{S \text{ cm}^{-1}} = 5.688 - 2.934 \times 10^4 T^{-1} + 5.678 \times 10^7 T^{-2} - 4.268 \times 10^{10} T^{-3} \quad (1)$$

The standard deviation of the relative values measured from the regressive equation (1) is $\sigma = 0.002$.

Table I

The values of conductivity and E_{corr} of CaMgSi₂O₆ melt

$\frac{T}{K}$	$\frac{\kappa}{S \text{ cm}^{-1}}$	$\frac{E_{\text{corr}}}{\text{kJ mole}^{-1}}$	$\frac{T}{K}$	$\frac{\kappa}{S \text{ cm}^{-1}}$	$\frac{E_{\text{corr}}}{\text{kJ mole}^{-1}}$
1568	0.098	179.8	1731	0.287	132.7
1575	0.106	177.0	1750	0.316	128.8
1598	0.127	168.6	1764	0.336	126.2
1627	0.155	159.0	1768	0.343	125.4
1660	0.194	149.5	1781	0.362	123.1
1680	0.218	144.3	1793	0.380	121.0
1693	0.235	141.1	1797	0.387	120.4
1700	0.244	139.5	1801	0.394	119.7
1705	0.251	138.3	1805	0.403	119.0
1715	0.266	136.1	1843	0.463	113.2
1726	0.280	133.7	1875	0.519	108.8

The conductivity of CaMgSi₂O₆ has so far been measured by Kawahara et al. [4] and Ličko and Daněk [3]. The results presented in [4] differ by about 10% from those obtained in the present work. This difference can be attributed to incorrect calibration of the conductivity cell and the associated absolute measuring error. Within the given measuring error, the results of study [3] are identical with those of the present paper.

However, it should be admitted that the results of the measurements reported here can involve a certain absolute error due to deformation of the conductivity cell. A direct estimate of this error is obviously impossible, even though the cell was designed so as to minimize the deformation brought about by heating up. The free volume theory was therefore used to verify the correctness of the measuring values [5, 6].

Validity of the free volume theory was verified on the melts of the system CaO—MgO—SiO₂ in [7]. It is based on the calculation of the linear relationship

$$E_{\text{corr}} = E_{\kappa} + \alpha RT^2 + \frac{1}{2} RT = kR \left(\frac{T}{T - T_0} \right)^2 \quad (2)$$

where E_{κ} is the activation energy of conductivity, α is the coefficient of volume expansion of the melt in question, R is the gas constant, k is a proportionality coefficient dependent solely on the size of the ions present, and T_0 is the temperature at which the free volume starts to form in the melt, and is experimentally very close to transformation temperature. Derivation of equation (2) can be found in [6, 7]. Equation (2) can be solved iteratively by choosing T_0 so as to make it pass through the origin, or analytically, when one obtains the quadratic dependence of the function $1/E_{\text{corr}} = f(T^{-1})$. On substituting the experimental values of E_{corr} (cf. Table I) into this equation and applying regression, it is possible to determine the coefficients allowing T_0 to be calculated. The activation energy of conductivity, defined by the equation

$$E_{\kappa} = -R \left(\frac{d \ln \kappa}{d \frac{1}{T}} \right) = -2.303R \frac{d \log \kappa}{d \frac{1}{T}} \quad (3)$$

was calculated from the conductivity measurements by differentiating equation (1). The coefficient of volume expansion of $\text{CaMgSi}_2\text{O}_6$ melt, α , was calculated from the data in [8]. The calculated values of E_{corr} are listed in Table I.

The agreement of T_0 value calculated and the transformation temperature value determined experimentally thus justify the assumption that the conductivity values used in the calculation were correct and did not involve any extraordinary absolute error, of course within the experimental error of T_g determination. Table II lists

Table II

Transformation temperatures of $\text{CaMgSi}_2\text{O}_6$ glass according to various authors, and the value of T_0 calculated from the conductivity values measured

Laboratory	Method	T_g/K
ÚACH Bratislava	dilat.	1014
	DTA	1006
VVÚS Trenčín	dilat.	1023
	DTA	1008
VÚSH Brno	DTA	1018
according to [9]	calor.	1005
Mean value		1012 ± 7
T_0/K	conduct.	998

the values of the transformation temperature of the $\text{CaMgSi}_2\text{O}_6$ melt established independently in three laboratories by two different methods and compared with the T_0 value calculated from the conductivity values measured. The agreement was satisfactory which indicates that the conductivity values measured were correct. In view of this the conductivity values reported here for the melt of $\text{CaMgSi}_2\text{O}_6$ can be accepted as reliable ones and the melt can be recommended as a standard substance for conductivity measurements at temperatures above 1500 K.

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TAVENINA CaMgSi₂O₆ — REFERENČNÁ LÁTKA PRE VODIVOSTNÉ
MERANIA PRI TEPLOTÁCH NAD 1500 K

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Konduktivitu taveniny zloženia CaMgSi₂O₆ možno v teplotnom rozmedzí 1570—1880 K popísať rovnicou

$$\log \frac{\kappa}{S \cdot \text{cm}^{-1}} = 5,688 - 2,934 \cdot 10^4 \cdot T^{-1} + 5,678 \cdot 10^7 \cdot T^{-2} - 4,268 \cdot 10^{10} \cdot T^{-3}$$

so štandardnou odchýlkou nameraných hodnôt od regresnej rovnice $\sigma = 0,002$. Overenie správnosti nameraných hodnôt konduktivity sa uskutočnilo pomocou teórie voľného objemu porovnaním experimentálne stanovenej hodnoty transformačnej teploty s hodnotou T_0 vypočítanou na základe teórie voľného objemu. Vzhľadom na dobrú zhodu týchto hodnôt možno taveninu CaMgSi₂O₆ odporučiť ako referenčnú látku pre vodivostné merania pri teplotách nad 1500 K.

РАСПЛАВ CaMgSi₂O₆ — СТАНДАРТНОЕ ВЕЩЕСТВО
ДЛЯ ИЗМЕРЕНИЯ ПРОВОДИМОСТИ
ПРИ ТЕМПЕРАТУРАХ СВЫШЕ 1500 К

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Проводимость расплава составом CaMgSi₂O₆ можно в пределах температуры 1570 по 1880 К описать в виде уравнения

$$\log \frac{\kappa}{S \cdot \text{см}^{-1}} = 5,688 - 2,934 \cdot 10^4 \cdot T^{-1} + 5,678 \cdot 10^7 \cdot T^{-2} - 4,268 \cdot 10^{10} \cdot T^{-3}$$

со стандартным отклонением измеренных величин от регрессного уравнения $\sigma = 0,002$. Проверку правильности измеренных величин проводимости проводили с помощью теории свободного объема сопоставлением установленной экспериментальным путем величины трансформационной температуры с величиной T_0 , рассчитанной на основании теории свободного объема. Так как проводимые величины находятся в хорошем согласии, можно расплав CaMgSi₂O₆ рекомендовать к применению в качестве стандартного вещества для измерения проводимости при температурах свыше 1500 К.

W. V. BAECKMANN, W. SWENK: KATODNAJA ZAŠČITA OT KORROZII
(Katodická protikorozi ochrana).

495 str., Metallurgija, Moskva 1984.

Protikorozi ochrane materiálu se ve všech průmyslově vyspělých zemích věnuje stále větší pozornost. Mezi různými způsoby protikorozi ochrany zaujímá zvláštní postavení elektrochemická ochrana, využívaná především po snížení koroze kovových zařízení, která jsou ve styku s elektrolytem (voda, mořská voda, vlhká půda, tavenina apod.). Touto problematikou se zabývá uvedená kniha, kterou v německém originálu vydalo nakladatelství Verlag Chemie v roce 1980.

Úvodní část knihy rozebírá teoretické základy koroze kovů a způsob protikorozi ochrany. Zvláštní pozornost je věnována metodám praktického stanovení parametrů v systémech katodické ochrany. Další kapitoly se týkají konkrétních případů katodické protikorozi ochrany potrubí, podzemních nádrží, kabelů, aparatur v chemickém průmyslu, ohřivačů vody apod.