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Investigation of Thermal Expansion of a Glass–Ceramic Material with an Extra-Low Thermal Linear Expansion Coefficient

T. A. Kompan · A. S. Korenev · A. Ya. Lukin

Abstract The artificial material sitall CO-115M was developed purposely as a material with an extra-low thermal expansion. The controlled crystallization of an aluminosilicate glass melt leads to the formation of a mixture of β-spodumen, β-eucryptite, and β-silica anisotropic microcrystals in a matrix of residual glass. Due to the small size of the microcrystals, the material is homogeneous and transparent. Specific lattice anharmonism of these microcrystal materials results in close to zero average thermal linear expansion coefficient (TLEC) of the sitall material. The thermal expansion coefficient of this material was measured using an interferometric method in line with the classical approach of Fizeau. To obtain the highest accuracy, the registration of light intensity of the total interference field was used. Then, the parameters of the interference pattern were calculated. Due to the large amount of information in the interference pattern, the error of the calculated fringe position was less than the size of a pixel of the optical registration system. The thermal expansion coefficient of the sitall CO-115M and its temperature dependence were measured. The TLEC value of about $3 \times 10^{-8}\,\mathrm{K}^{-1}$ to $5 \times 10^{-8}\,\mathrm{K}^{-1}$ in the temperature interval from $-20\,^{\circ}\mathrm{C}$ to $+60\,^{\circ}\mathrm{C}$ was obtained. A special investigation was carried out to show the homogeneity of the material.

Keywords Interference field · Sitall · Standard dilatometer · Thermal expansion coefficient (TEC)

T. A. Kompan (✉) · A. S. Korenev · A. Ya. Lukin
D.I. Mendeleev Institute for Metrology, Moskovsky av. 19, St. Petersburg 190005, Russia
e-mail: T.A.Kompan@vniim.ru

1 Introduction

Materials with a thermal linear expansion coefficient (TLEC) close to zero are necessary in many fields of technology where a high dimensional stability and independence of dimensions on temperature are required.

Let us briefly discuss the physical reasons why some groups of materials have extra-low TLEC values. Different mechanisms can contribute to thermal expansion: magnetic interactions, conduction electrons, and defects in solids. In a number of cases, the anharmonism constant of lattice vibrations can have a minus sign. Due to the mutual compensation of contributions to thermal expansion, the TLEC can become very small in a certain temperature range and, in some cases, even take negative values. Thus, in the process of thermal expansion, the TLEC values of germanium, silicon, and some semiconductors from the Group $A^{III}B^{V}$ change their sign twice: the first time near 50 K to 100 K to the negative, and then near 10 K to 20 K. The Invar alloys are another well-known case. They present a substance where the positive contribution of lattice anharmonism is compensated by a negative contribution from magnetostriction. Some microinhomogeneous materials form a separate group of substances with a low TLEC. They include, for example, glass–ceramic materials—sitalls—whose TLEC values depend on the relation between the expansion coefficients of the crystal and glassy phases, and may have any specified values, including those close to zero.

Technical sitalls are products of the crystallization of specially-composed glasses that can turn into microcrystal materials in the process of heat treatment. Throughout their whole volume, the very fine crystals are uniformly distributed, have direct contact with each other, and are connected by a thin film of residual glass. Controlling the dimensions, density, and chemical-mineralogical composition of the crystals by changing the temperature and duration of heat treatment, one can regulate the process of crystallization and obtain sitalls with the prescribed properties.

The sitalls with a low TLEC are generated mainly in the systems $Li_2O–Al_2O_3–SiO_2$ and $MgO–Al_2O_3–SiO_2$ with the addition of TiO_2. Sitalls based on lithium-aluminosilicate glasses have β-spodumen, β-eucryptite, and β-silica as the main crystal phases, and have a lower TLEC than the initial glasses. The CO-115M transparent sitall with a TLEC value close to zero has been synthesized on this principle. Its finest crystals—β-eucryptites—are separated from each other by the thinnest glass film. The TLEC of this material is close to zero due to the decrease of Li_2O content and the increase of the amount of glassy phase. By thorough selection of the composition and technology, we have managed to obtain a material with a TLEC of $3 \times 10^{-8}\ K^{-1}$ to $5 \times 10^{-8}\ K^{-1}$, which practically has no temperature dependence in the range from $-20\ °C$ to $+60\ °C$.

The CO-115M sitall is transparent, a property which is attained by special heat treatment when the dimensions of the crystallites in this material become much smaller than the optical wavelength. The material is highly homogeneous, and the refractive index is close to that of glass.

The above properties of this sitall make it very attractive for manufacturing weight-reduced astro-optics, and it has broad application in other fields where high dimensional stability is required, including the manufacture of standard specimens of TLEC for the verification of precise dilatometers.

The results of our investigations of the TLEC of CO-115M optical sitall will be discussed.

2 Measurements

2.1 Specimens

The specimens were prism-shaped with heights of 20 mm and 30 mm and prism sides of 15 mm width (Fig. 1). Each specimen had three equally spaced supporting surfaces, each having an area of not more than 0.5 mm^2. The non-parallelism of the specimen end faces was 15$''$ to 35$''$. There was an axial bore of 6 mm to 8 mm diameter through the center, into which a temperature-measuring transducer was inserted.

The material for the interference plates was selected on the basis of the thermal expansion of the specimen under study and the working temperature range. Transparent quartz glass interference plates were used in this experiment.

To determine the TLEC value, two specimens with lengths of 20 mm and 30 mm were investigated in the temperature range from −80 °C to +120 °C.

To study the TLEC homogeneity of the CO-115M sitall, the TLEC values were measured for specimens cut from different layers of the ingot.

2.2 Procedures

2.2.1 Thermal Expansion

The TLECs of CO-115M sitall specimens were measured by means of a standard dilatometer [1] in the temperature range from −80 °C to +120 °C using an

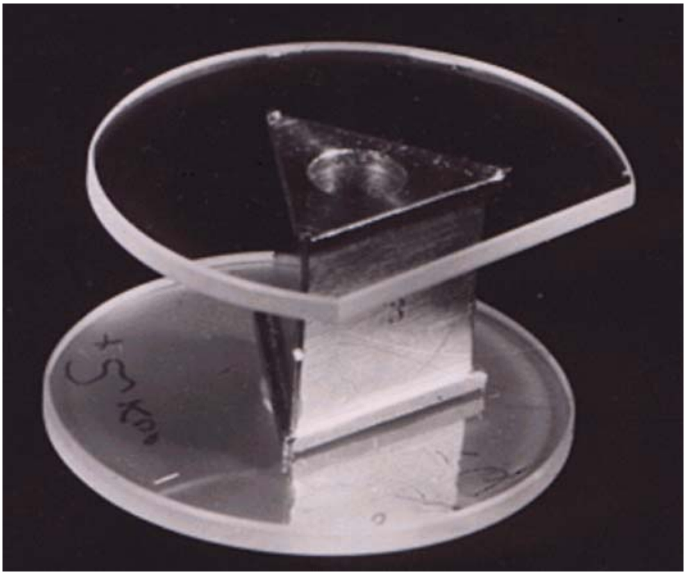

Fig. 1 Specimen under study with interference plates

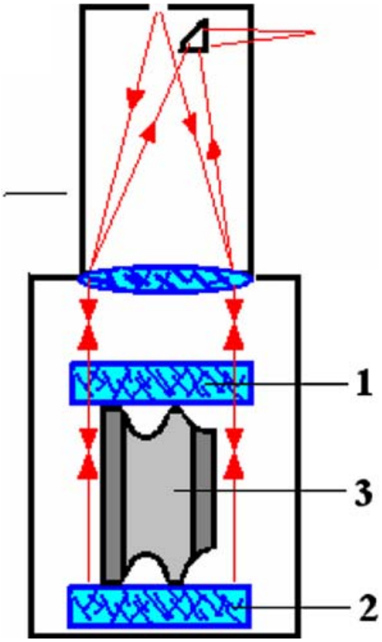

Fig. 2 Fizeau interferometer diagram: 1, 2—interference plates; 3—specimen under study

interferometric method. The specimen to be measured was placed between two interference plates forming a Fizeau interferometer with a wedge angle of about 30° (Fig. 2). In this case, the specimen between the interference plates was illuminated with monochromatic light that formed a system of fringes (the so-called fringes of equal thickness) parallel to the wedge angle. The length of the specimen changed with temperature, and hence, the path-length difference of the interfering rays changed, which resulted in a shift of the interference fringes (Fig. 3). By measuring the fringe shift, we could determine the specimen length change due to its temperature variation.

The method of intensity reading from the whole interference field [2,3] was applied to ensure the required measurement accuracy. High-precision matrix CCDs (video cameras) with fast-acting devices to input images into a computer with appropriate data processing algorithms were used as recorders. Reading of the information from the whole interference pattern made it possible to calculate the phase and the fringe period at all points of the interference field, to measure the inclination angle of the fringes, and to eliminate the uncertainties due to possible shifting of the specimen in the process of temperature changes and deformations of the setup. The reading of the video information was done using specialized software intended for this experiment and data analysis.

The temperature of a specimen under study was measured using a platinum resistance thermometer located in the axial bore of the specimen.

2.2.2 Uncertainties

The TLEC of materials is determined by measuring the length change and the temperature variation of a specimen under study, and by subsequent calculation of the values

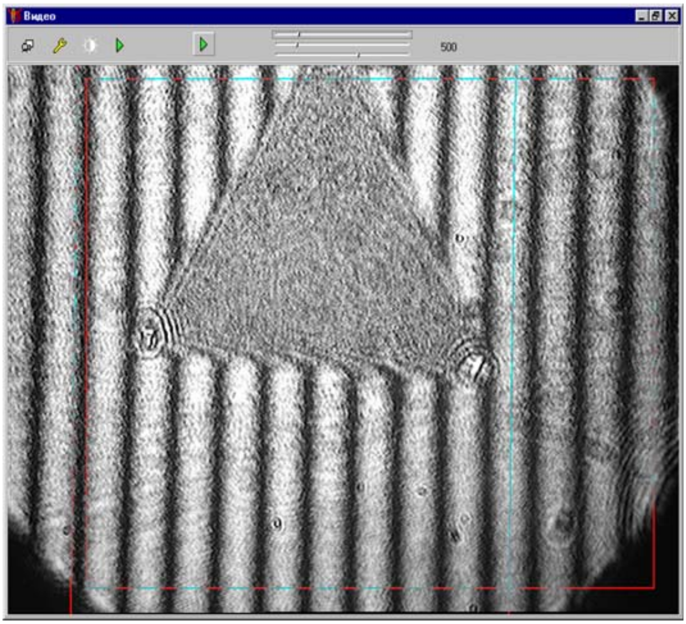

Fig. 3 Interference pattern with a specimen

of thermal expansion. During TLEC measurements, the interference dilatometers have uncertainties of both a systematic and random nature.

When measuring the length change by calculating the number of interference fringes passing with illumination from the light of a single spectral line, the elongation of the specimen when the temperature changes from T_1 to T_2 can be calculated by the formula,

$$\Delta L = N\lambda_{\text{vac}}/2 = (\Delta N + \varepsilon_1 + \varepsilon_2)\lambda_{\text{vac}}/2 \tag{1}$$

where λ_{vac} is the wavelength in vacuum; ΔN is the number of passing interference fringes when the temperature changes from T_1 to T_2; ε_1 is the fringe fraction at temperature T_1, counted from the point in the middle of the dark fringe taken as zero; and ε_2 is the fringe fraction at temperature T_2, counted from the point in the middle of the dark fringe taken as zero.

Since the elongation uncertainties are the most significant components in the TLEC measurement uncertainty in the investigation of the TLEC of materials with a low thermal expansion, Table 1 presents the estimates of these particular components.

The average TLEC values in the constant temperature range are determined by the formula:

$$\alpha_{\text{aver}} = \Delta L/(L_{20}\Delta T) \tag{2}$$

Table 1 Uncertainty components of the elongation measurement

No.		Source of uncertainty	Uncertainty value $U(x_i)$	$\frac{\partial f}{\partial xi} \times u(xi)$	$u:(\Delta \mathrm{L})$	µm	Type
1	$S_{\Delta \mathrm{Li}}$	Determination of fractional parts of interference orders	0.005 fringe	$\lambda/2$	$0.005 \times \lambda/2 \times \sqrt{2}$	0.0023	A
2	$S_{\Delta \mathrm{Lp}}$	Location with reference to the chosen point of a specimen	0.002 fringe	$\lambda/2$	$0.002 \times \lambda/2 \times \sqrt{2}$	0.001	A
3	$S_{\Delta \mathrm{Lw}}$	Changes in a wedge angle	$\delta P = 2.5 \times 10^{-4}$	$\delta P \times \lambda/2$	$(2.5 \times 10^{-4}) \times \lambda/2 \times \sqrt{2}$	0.00011	A
4	$S_{\Delta L\nu}$	Instability of radiation frequency		$(\Delta\lambda/\lambda) \times L$	$[(1 \times 10^{-8}) \times L\sqrt{2}]/\sqrt{3}$	0.00012	A
5	ϑ_{λ}	Uncertainty of wavelength determination	1×10^{-8}	$(\Delta\lambda/\lambda) \times L$	$1 \times 10^{-8} \times L\sqrt{2}$	0.00021	B
6	ϑ_{n}	Index of air refraction	$\Delta n/n = 1 \times 10^{-9}$	$\Delta n \times L$	$1 \times 10^{-9} \times L \times \sqrt{2}$	0.00014	B
		Standard uncertainty	$u_{\mathrm{A}(\Delta \mathrm{L})} = 0.0028$ to 0.038				
			$u_{\mathrm{B}(\Delta \mathrm{L})} = 0.0013$ to 0.024				

where L is the specimen length at $T = 20\,°\mathrm{C}$ and ΔL is the specimen elongation when its temperature is changed by ΔT. The accuracy of the TLEC value depends on the uncertainties of the quantities from Eq. 2. The average TLEC dispersion for the constant temperature range can be calculated from the formula,

$$S^2_{\alpha\text{aver}} = (\partial\alpha_{\text{aver}}/\partial L_{20})^2 S^2_{L20} + (\partial\alpha_{\text{aver}}/\partial\Delta L)^2 S^2_{\Delta L} + (\partial\alpha_{\text{aver}}/\partial\Delta T)^2 S^2_{\Delta T} \quad (3)$$

After the necessary calculations, we have

$$S^2_{\alpha\text{cp}} = (\alpha_{\text{cp}}/L_{20})^2 S^2_{L20} + (1/L_{20}\Delta T)^2 S^2_{\Delta L} + (\alpha_{\text{cp}}/\Delta T)^2 S^2_{\Delta T} \quad (4)$$

Thus, to determine the measurement uncertainty of the average TLEC in the set temperature range, it is necessary to know the uncertainties of the following: measurement of the specimen length at $T = 20\,°\mathrm{C}$, elongation of the specimen, and the temperature increment of the specimen corresponding to the given elongation. Analyses of the uncertainty components of elongation and of the temperature measurements using a standard dilatometer allow estimation of their value. The TLEC measurement uncertainty is calculated on the basis of the obtained estimates of the uncertainty components using Eq. 4.

As the average TLEC measurement uncertainty does not only depend on the measurement uncertainties of the specimen length change and of its temperature, but also on the TLEC value of the material under study and the temperature range for which the average TLEC has been calculated, the uncertainties of the measurement result obtained by means of a standard dilatometer is calculated for materials with different TLECs.

Due to the application of modern hardware and software capabilities, as well as the multiple parameter method of processing the interference pattern, the dilatometer makes it possible to measure the length change of a specimen under study with a standard uncertainty, estimated by a Type A method, $u_{\mathrm{A}} = 0.0005\,\mu\mathrm{m}$ to $0.001\,\mu\mathrm{m}$, and with a temperature uncertainty $u_{\mathrm{A}} = 0.005\,\mathrm{K}$ to $0.05\,\mathrm{K}$ over a wide temperature range. The measured temperature range is 90 K to 600 K; the measured TLEC range is $0.01 \times 10^{-6}\,\mathrm{K}^{-1}$ to $25 \times 10^{-6}\,\mathrm{K}^{-1}$. The standard uncertainty of the TLEC measurement result estimated by a Type A method with three independent measurements for the temperature range of 100 K is $0.05 \times 10^{-8}\,\mathrm{K}^{-1}$. The standard uncertainty of the TLEC measurement result estimated by a Type B method (for $P = 0.99$) is $0.03 \times 10^{-8}\,\mathrm{K}^{-1}$.

3 Results

Two sitall specimens with lengths of 20 mm and 30 mm were investigated in the temperature range from $-80\,°\mathrm{C}$ to $+120\,°\mathrm{C}$. The results of dilatometric investigations were approximated using cubic splines with reduced curvature, minimizing the weighted standard deviation. The splines were constructed on the basis of elongation values at different temperatures meeting the continuity conditions of the first and second derivatives at the points of approximation [4].

Table 2 Average measurement results of the CO-115M sitall specimens

$T\,(^\circ\mathrm{C})$	$\Delta L/L \times 10^5$	$\alpha \times 10^6\,(\mathrm{K}^{-1})$
−60	9.201	−0.115
−50	6.134	−0.088
−40	3.729	−0.062
−30	2.212	−0.044
−20	1.258	−0.031
−10	0.61	−0.02
0	0.213	−0.011
10	0.026	−0.003
20	0	–
30	0.085	0.008
40	0.229	0.011
50	0.422	0.014
60	0.785	0.02

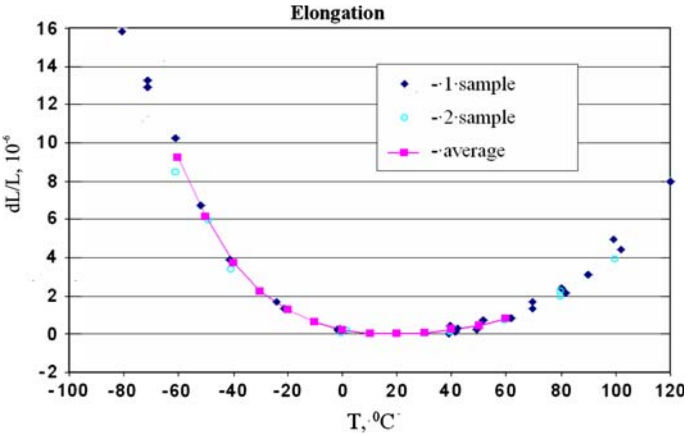

Fig. 4 Elongation of sitall CO-115M in the temperature range from −80 °C to +120 °C (data for two samples and average values)

The average measurement results of the CO 115-M sitall specimens are presented in Table 2. The TLEC measurement uncertainty was $5 \times 10^{-10}\,\mathrm{K}^{-1}$ to $1 \times 10^{-9}\,\mathrm{K}^{-1}$. Figures 4 and 5 show the temperature-elongation diagram and temperature-average linear expansion coefficient diagram, respectively. The figures demonstrate that the material expansion was minimal in the temperature range from 20 °C to 0 °C.

More than 30 blocks of the given material with a diameter of about 800 mm and a height of about 1,000 mm were used to study the inhomogeneity of CO-115M sitall. The specimens were cut from different parts of the cast block: upper part, middle, and bottom, as well as from the periphery and central part. The measurements provided data for the average TLEC values in the temperature range from 0 °C to 20 °C and data for the TLEC inhomogeneity of each cast block. Table 3 presents the TLEC measurement results of the sitall specimens cut from different parts of a single cast block. The measurement results demonstrate that the TLEC inhomogeneity of one melting

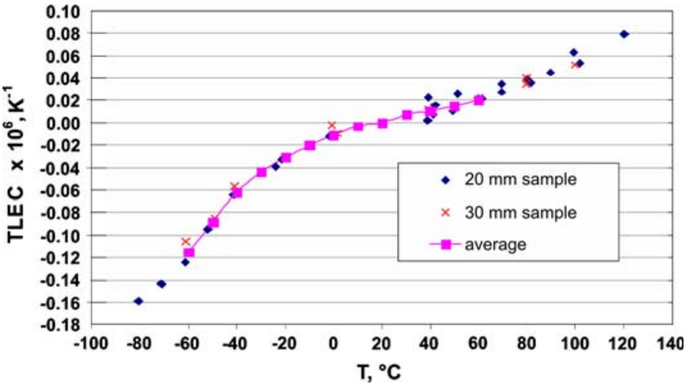

Fig. 5 Temperature dependence of the TLEC value of sitall CO-115M in the temperature range from $-80\,^\circ$C to $+120\,^\circ$C (data for two samples and average values)

Table 3 TLEC measurement results of the sitall specimens cut from different parts of a single cast block

Block No. 2			
Specimen No.	$\alpha_{\text{aver}} \times 10^8$ (K^{-1})	Average $\alpha_{\text{aver}} \times 10^8$ (K^{-1})	Uncertainty $u_A \times 10^8$ (K^{-1})
003/01 (upper part)	−0.48	−0.51	0.031
	−0.54		
	−0.52		
003/02 (middle–center)	−0.52	−0.55	0.046
	−0.58		
004/18 (middle–periphery)	0.71	0.27	0.391
	0.15		
	−0.05		
005/18 (bottom)	−0.13	−0.29	0.233
	−0.46		

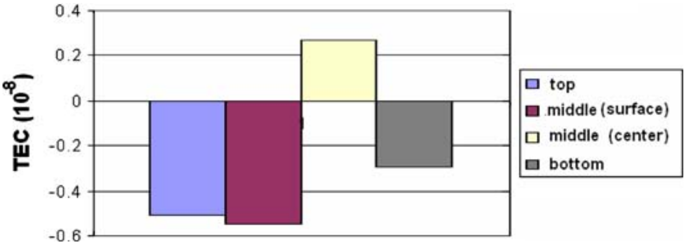

Fig. 6 Homogeneity test: TEC values for different samples cut from various parts of the bulk sitall ingot

of the material does not exceed $1 \times 10^{-8}\,\text{K}^{-1}$. Figure 6 shows the TLEC deviation of each specimen from the average TLEC inside one cast sitall block. The obtained results enable us to come to the following conclusions:

- the TLEC value of the material does not exceed ±1 × 10^{-7} K^{-1} in the temperature range from 0 °C to 20 °C for all meltings studied; and
- the TLEC inhomogeneity in the block does not exceed ±1.5 × 10^{-8} K^{-1}.

The investigations were performed with the purpose of finding an opportunity to use CO-115M sitall as a constructional material for the production of astronomical mirrors, specifically, for the production of a 10 m mirror for the Large South Africa Telescope. At the same time, they served as methods for the technological control and certification of this material for TLEC when manufacturing the components of the given mirror [5]. The measurement results enabled us to prove the high stability of the TLEC of the given material both inside each melting and for the material as a whole, which proved the fitness of this material for the specified purpose.

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