

# THERMAL EXPANSION OF SOLIDS: RECENT RESEARCH AND STANDARD MATERIALS

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**Abstract:** The paper describes the metrological activity in D.I. Mendeleev Institute for Metrology (S.-Petersburg, Russia) in the field of dilatometric research of solids. The main attention is paid to standard reference materials and standard samples of Thermal Expansion.

**Keywords:** PIPELINE STEEL, PROCESSING, MICROSTRUCTURE, TEXTURE

## 1. Introduction

Thermal expansion of solids is a general property of condensed materials. It is based on the fundamental principle of condensed matter structure: on the asymmetry of the attractive forces between particles (atoms), constituting macroscopic bodies. Whereas the distance between the particles is determined by force balance, potential minimum in the balance point stays asymmetric, therefore, with temperature increase, the particles are displaced towards the flat side of the potential well.

From thermal expansion research one can obtain information about inter-atomic forces as well as estimate anisotropy and anharmonicity of the inter-atomic interaction in solids. Accurate measurement of the temperature coefficient of thermal expansion is required for fundamental studies in solid state physics (e.g. point defect formation).

The thermal expansion usually is described by Thermal Expansion Coefficient (TEC). In its turn, TEC may be formalised by one of possible ways:

$$\alpha = dL / L dT \quad (\text{differential})$$

$$\alpha_{av} = \Delta L / L \Delta T \quad (\text{averaged over temperature interval})$$

$$\beta = dV / V dT \quad (\text{volume expansion coefficient})$$

First one is used preferentially in scientific research, the second variant of TEC is more convenient for practical purposes, e.g. in industry, and the last concerning the relative volume expansion. The physical dimension of TEC is  $K^{-1}$ . The various authors may assume different variant of

TEC formalisation and this should be take into account.

Coefficient of thermal expansion is related to the other thermodynamic parameters, including heat capacity, that follows from the Gruneisen's relation [1]

$$\beta = \gamma \frac{C_v}{V} \chi_T \quad (1)$$

where  $\beta$  – is volumetric coefficient of thermal expansion;

$\gamma$  - Gruneisen parameter, describing Debye temperature variation with volume change;

$V$  - molecular volume

$C_v$  - heat capacity at constant volume

$$\chi_T = - \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \quad \text{- isothermal compressibility.}$$

Temperature dependence of thermal expansion coefficient can be determined from the expression above. In Gruneisen approximation  $\gamma$  does not depend on temperature, whereas  $\chi$  and  $V$  vary

slow with temperature, which means that dependence of TEC on temperature is mostly determined by course of temperature of heat capacity. Therefore coefficient of thermal expansion tends to zero as  $T \rightarrow 0$  K, and tends to a constant value for higher temperatures. In some cases, structural and phase transitions can cause a sharp change of sample dimensions.

Magnitudes of TEC for the most materials vary within a factor of ten at room temperature as a result of the general laws for the condensed matter interaction pattern. Proximity of TEC values of various materials and their weak dependence on the history and purity of material emphasize the fundamental character of the quantity and also its relation to general material parameters and the structure of material. Therefore, thermal expansion is an important and informative parameter of the solid, which is related to the thermodynamical parameters (Helmholtz energy, enthalpy) and the structural parameters (phonon spectrum, lattice anharmonicity, defects) of the material.

On the other hand TEC should be taken into account whenever one deals with wide range of temperatures: from cryogenics to solid state technology. For instance, coefficient of thermal expansion of the material for the telescope mirror has to be controlled up to  $10^{-8}$  K. Dilatometer data is also required for vacuum and solid state electronics, where different materials junctions are used, for building heterojunctions in optoelectronics, because normal operation of heterojunction devices are limited by strain accumulation due to materials TEC mismatch. These and other applications require high precision TEC determination in a wide range of temperatures.

## 2. The apparatus and method of measurements

Coefficients of thermal expansion for modern artificial materials, including custom made ones, in contrast, can vary over a wide range between  $0.01 \cdot 10^6$  and  $50 \cdot 10^{-6} K^{-1}$ . There are many types of dilatometers dealing with different scientific and practical problems of materials. Any of those dilatometers has got its constructive and operating features. Different TEC determination technique is used for different purposes.

It can be problematic to take into account all of the entities that influence the TEC measurement precision. Therefore for calibration of dilatometers special standard reference materials (SRM) with different physical properties are used.

Typically, a dilatometer should be calibrated using materials similar to those to be studied in specific measurements. Using similar kinds of materials provides realistic examination under near-real conditions in order to minimise possible side effects contributing to the measurement uncertainty. This explains the necessity to find suitable reference materials for TEC standards with different TEC values and various physical properties.

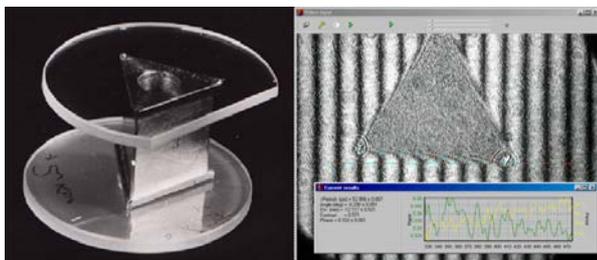
The TEC measurement includes measurements of sample length, elongation and interval of the temperature change. Methods of measurements for SRM certification have to provide accuracy, comparable with the highest accuracy achievable for every kind of measurements.

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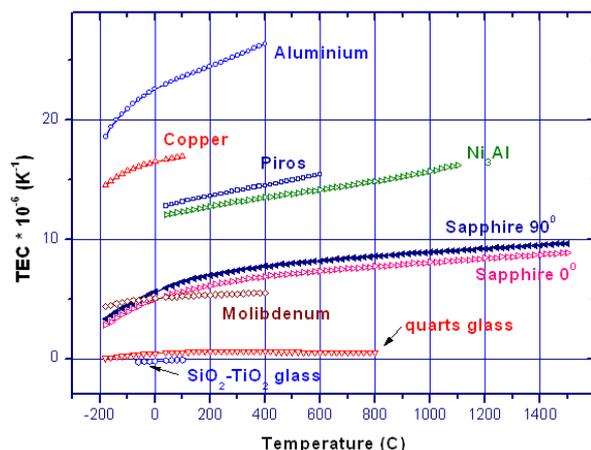
In Russia values TEC of SRM materials have been obtained using high precision interference dilatometers from "D.I.Mendeleev Institute for Metrology", that provide standard deviation of the TEC value up to  $0,5 \cdot 10^{-9} \text{ K}^{-1}$  in 100 degree temperature range [2]. Stability of the properties of the reference materials and standards is given special attention, with highest priority to the TEC values stability.

Measurements in VNIIM dilatometers are based on analysis of the interference fringe pattern. Special algorithm is used for interferogram processing, that provides detection of phase shift value up to  $10^{-3}$  [3]. At fig 1. the test sample with the interference plates is shown along with the experiment monitor screenshot, displaying current interference pattern and experiment data record.



**Fig1.** Left: sample under investigation with the interferometric plates; Right: Experiment monitor view shows interferometric pattern and the real-time plot of experiment parameters.

The technique, mention above, allowed to develop a set of standards with different physical properties for use in a wide range of temperatures between 90 and 1800 K to meet all customer requirements. As a rule, the reference materials have to be clear, chemically inert and homogeneous, neither changing their properties with time, nor having any phase transitions in the given temperature range. Platinum, copper, single crystalline aluminum oxide, molybdenum, aluminum, different sorts of fused silica, multi-alloys are used for that purpose. The TEC values of those materials, depending on the temperature, are shown in fig 2.



**Fig.2** TEC value for various materials as a function of temperature

### 3. Results

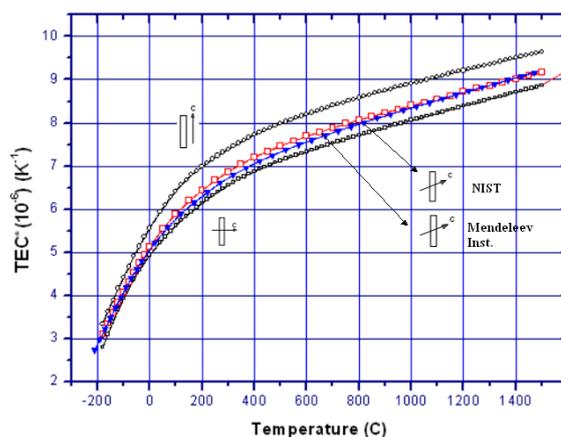
Recent years the samples made of the specially oriented single crystalline sapphire, imitating the LEC of corundum ceramics, are the most popular [4].

Single crystal sapphire is an anisotropic crystal. The crystal belongs to a trigonal syngony, to a space group 3m. The TEC value along the crystal axis of  $\text{Al}_2\text{O}_3$  differs from that for the transverse direction ( $\alpha = 5.62 \cdot 10^{-6} \text{ K}^{-1}$ ;  $\alpha_t = 6.44 \cdot 10^{-6} \text{ K}^{-1}$  in the temperature range 20-100°C). Length gauge made of sapphire do not change there dimensions during thermal cycling. So, the properties of crystal sapphire make it a multipurpose reference material. It does not undergo any phase traditions in the temperature range to 2000 K.

Nowadays the push-rod dilatometers for high temperature TEC measurement are spread worldwide. Those dilatometers are produced by the world's leading corporations. They have a kinematics system made of aluminum oxide ceramics. To determine the uncertainty of the dilatometer's own extension, TEC reference materials should be the same as that of the kinematics system or to have TEC value as close as possible. However ceramic length standards do not meet requirements on accuracy, because their properties are less repeatable than those of single crystal. A single crystal standards with the length axis aligned at the angle of  $59^\circ$  to the crystal C axis are the best for this purpose, as their TEC value is close to TEC of corundum ceramics.

On the other hand that kind of orientation toughens the requirements for the sample orientation with respect to the crystal C axis. To achieve TEC standard uncertainty value of  $5 \cdot 10^{-8} \text{ K}^{-1}$ , alignment accuracy of  $\pm 2^\circ$  is required for  $59^\circ$  alignment. Production and wide spread of these standards became possible because of successful cooperation with the material scientists from Russian Academy of Sciences who developed the growth method of profiled sapphire single crystal.

Next figure 3 show the investigation results. The data shown are the TEC of single crystal sapphire for various orientations. Along with the data from D.I.Mendeleev institute the NIST data are also shown for comparison.



**Fig.3** Dependence of TEC of single crystal sapphire for different orientations. The two curves for  $59^\circ$  orientation are the data from NIST and from D.I.Mendeleev Institute.

It can be seen that scattering of the single crystal TEC data from different authors with regards to the data in this paper fall within uncertainty range of the dilatometer used.

Alumosilicate based pyroceramics CO-115M (Lytcarino, Russia), can be provided as another example of thoroughly studied ultraslow TEC material. This ceramics include the nanocrystals of  $\beta$ -spodumene,  $\beta$ -silica and  $\beta$ -eucryptite as a phase, reducing TEC of initial glass. Transparency of alu-

mosilicate is achieved by thermal treatment, when crystalline dimensions become significantly smaller than wavelength.

Alumosilicate TEC measurements were performed using the Institute's high precision interference dilatometers according to the measurement technique, providing average TEC measurement standard deviation in the hundred degree range of  $0,2 \cdot 10^{-8} \div 0,5 \cdot 10^{-8} \text{ K}^{-1}$  [5]. More than 30 slabs of this material have been studied. Fig. 4 shows typical temperature dependencies of TEC for  $-60 \div 100 \text{ }^\circ\text{C}$  temperature range. One can see that the material almost do not change it's size around room temperature.

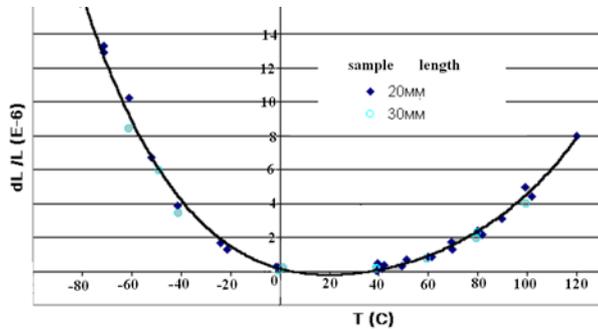


Fig. 4 Temperature dependence of expansion of the CO115-M alumosilicate samples.

The special attention was drawn to homogeneity of material. Test samples were cut out of different parts of the block: upper part, middle, lower part, edge and center. Figure 5 illustrates TEC scattering within the slab.

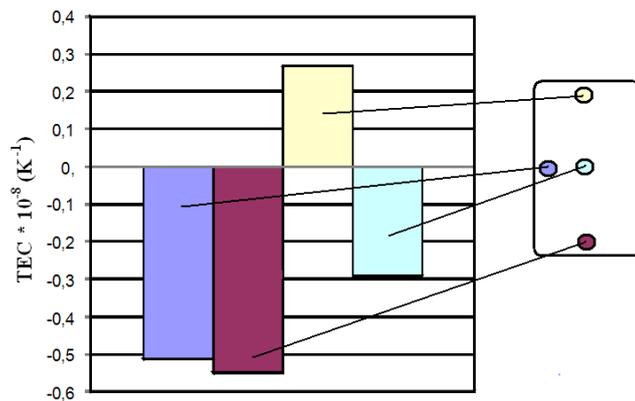


Fig. 5 Homogeneity of TEC inside the CO115-M alumosilicate slab

Low TEC value and time stability of CO115M alumosilicate allowed to use this material for producing the mirror of the Southern African Large Telescope, and also in metrology as low TEC reference material [6] (Fig.6).

#### 4. Conclusions

D. I. Mendeleyev Institute for Metrology has resources for precise TEC measurements, develops and supplies reference materials with certified properties.

Everybody is welcome to collaboration.

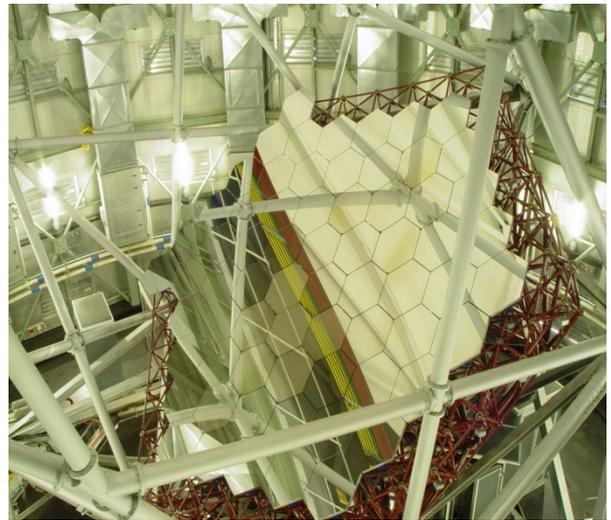


Fig. 6. 10-meter mirror of SALT assembly. Mirror elements made of ultralow TEC material. TEC value and material inhomogeneity was supervised by D.I. Mendeleyev institute for Metrology.

#### 5. References

- [1] E. Gruneisen, Handbuch der Physik, 1926,10, 1.
- [2] A. I. Pokhodun, T. A. Kompan, N. A. Sokolov, et al "The Upgraded State Primary Standards for Units of Thermophysical Quantities", *Izmeritelnaya Tekhnika*, No. 8, 55 (2009)
- [3] T.A. Kompan, A.S. Korenev, A.Ya. Lukin, "An automatic system for dilatometric measurements with the multiparametrical data processing from the of interference pattern field", *Izmeritelnaya Tekhnika*, No. 6, 31 (2001)
- [4] Kompan T., Korenev A., Lukin A., Antonov P.,V. Krymov "Profiled single cristal sapphire – new reference material dilatometry " *Bulletin of the Russian Academy of Sciences: Physics*, 2004, v. 68, № 6, p.895-898
- [5] Kompan T., Korenev A., Lukin A. "Investigation of Thermal Expansion of a Glass-Ceramic Material with an Extralow Thermal Linear Expansion Coefficient", [International Journal of Thermophysics](#) 2008, Volume 29, Number 5, p. 1896-1905.
- [6] O. Ponin, A. Sharov, I. Galyavov, T. Kompan, J. Swiegers, A. Swat, in *Proc. of SPIE "Large Ground-Based Telescopes"*, SPIE, Bellingham, 2003 v.. 4837, part 1, pp. 795-804.