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Thermal Expansion in Metal/Lithia–Alumina–Silica (LAS) Composites[1]

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Lithia–alumina–silica (LAS) with metallic dispersions offers a new approach toward near-zero, isotropic, thermal expansion composites. The metallic phase contributes a positive coefficient of thermal expansion (CTE) to the negative CTE of the glass/ceramic matrix. In addition, the metal will increase the electrical and thermal conductivities over those of the matrix alone. The LAS system offers tailorable negative CTEs and light weight compared to other negative CTE ceramics. The most negative CTE phase is crystalline β-eucryptite, whose proportion in an initially glassy matrix can be controlled by heat treatment. Dispersed metal powders were both hot-pressed and cold-pressed and sintered together with LAS matrices prepared by sol gel methods. Super Invar powder was studied for its minimal CTE mismatch, while titanium powders offered a compromise between light weight and low CTE. An ultralow-expansion (ULE) glass- and linear variable differential transducer (LVDT)-based differential dilatometer was developed for rapid screening of compositions, while a double-laser Michelson interferometer was used for precise near-zero CTE measurements. The reinforced β-eucryptite glass/ceramic matrix exhibited both a U-shaped $\Delta L/L$ curve with temperature and some thermal hysteresis, depending on the fabrication and heat treatment sequences. The temperature of the zero-CTE portion of this curve was found to change with increasing titanium powder content. Results are also given for mixtures of Super Invar powders in ULE glass and β-eucryptite matrices. Negative CTEs in a LAS matrix above ambient temperatures were more difficult to obtain than below, although the use of petalite (high-silica LAS) appears promising.

KEY WORDS: ceramics; composites; eucryptite; lithia–alumina–silica; thermal expansion.

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1. INTRODUCTION

The objective of this project was to develop a strong lightweight material with a zero coefficient of thermal expansion (CTE) in all directions (isotropic) over the temperature range of ±200°C. Such a composite would greatly improve the thermal conductivity, thermal shock resistance, and fracture toughness over present near-zero CTE glasses and ceramics. The basic approach was to combine negative (mainly ceramic) and positive (metallic) CTE materials.

Stringent dimensional stability requirements are called for in mirrors and general optics, sensors, microwave components, and antennas. In many optical systems, such as infrared telescopes [1], the ratio of thermal conductivity (K) to CTE, the uniformity of CTE, and the infrared absorptivity are critical. Tradeoffs are required between beryllium (high K, good infrared reflectivity, moderate CTE, and poor CTE uniformity) and fused silica (low K, high infrared absorptivity, and good CTE uniformity). An opaque mirror substrate with a high K and a zero average CTE from fabrication to use temperature would find considerable application in cooled optical systems.

Previous studies defined the materials options and approaches [2–5]. The work of Suh et al. [4] at the Massachusetts Institute of Technology, supported by our CTE measurements, concentrated on theoretical analyses and experimental work with heavy composite systems. These included negative-CTE ceramics based on the Ta–W–O and Ta–V–O systems mixed with metals such as Super Invar and copper. Major conclusions were that fabrication conditions (e.g., time, temperature, pressure, particle sizes) must be carefully controlled in order to minimize chemical reactions between the constituents and that differential CTEs must be kept low to minimize microcracking.

The lithia–alumina–silica (LAS) system was selected here to provide the negative-CTE ceramic phase because of its low specific gravity (2.3) and its ability to provide a volumetric negative CTE. Because of their excellent thermal shock resistance, LAS ceramics are prime candidates for catalytic converters, regenerators, flow separator housings, and mirror blanks. They can easily be fabricated into complex shapes by a number of ceramic forming techniques. Whereas LAS includes higher silica phases (e.g., spodumene, petalite), Whereas LAS includes higher silica phases (e.g., spodumene, petalite), the most negative CTEs are reported for β-eucryptite ($Li_2O \cdot Al_2O_3 \cdot 2SiO_2$).

The CTE of a two-phase mixture of a spherical metal dispersoid (d) in a hydrostatic stress state in matrix (m) was given by [4]

$$\alpha_c = \alpha_m + \frac{3(1-\nu_m)(\alpha_d-\alpha_m)\,V_d}{2(E_m/E_d)(1-2\nu_d)+2(1-2\nu_m)+(1+\nu_m)} \qquad (1)$$

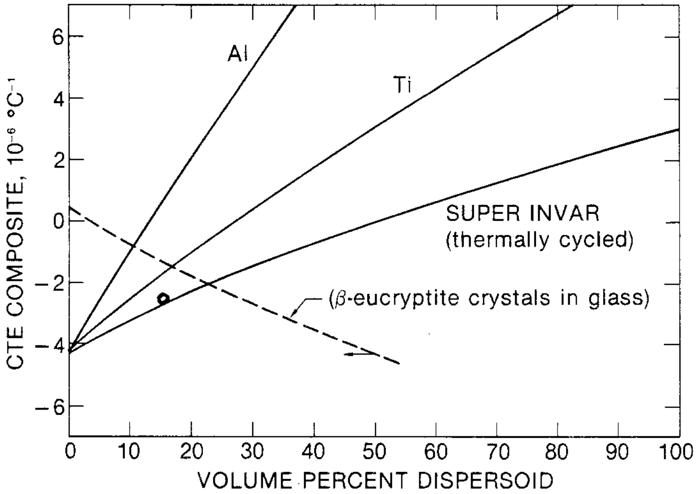

Fig. 1. Variation of predicted CTE with volume percentage of metallic dispersoid in a 50/50 mixture of β-eucryptite glass and crystals.

where α, E, and ν, respectively, represent the CTE, the elastic moduli, and the Poisson's ratios of the matrix or dispersoid, and V_d is the volume fraction of the dispersoid. Figure 1 illustrates some predictions based on a value of CTE of crystalline β-eucryptite of -8×10^{-6} °C^{-1} [6]. Due to crystalline anisotropy (α along the "c" axis is -17.6×10^{-6} °C^{-1}, whereas along the "a" axis, it is $+8.2 \times 10^{-6}$ °C^{-1}), highly crystallized β-eucryptite materials easily form microcracks and have a low strength. The solution adopted here was to settle for a less-negative CTE matrix by using a com-

Table I. Properties of Constituents (20–180°C)

Material	Poisson's ratio (ν)	Young's modulus (GPa)	CTE (10^{-6} °C^{-1})
Al (matrix)	0.33	68.9	22.7
Ti (matrix)	0.33	113	9.4
Invar (dispersoid)	0.26	147	0.7
Super Invar (dispersoid)	0.23	148	−0.1–4
Quartz (dispersoid)	0.17	73.1	0.6
ULE (dispersoid)	0.17	68.9	0.03
LAS (dispersoid)	0.26[a]	87[a]	Variable

[a] Estimated value.

Table II. Radial Stress at the Interface

		S_R (MP$_a$)
Al_2O_3	In glass [8]	$0.25\,\Delta T$
Super Invar	In ULE	$0.26\,\Delta T$
Super Invar	In LAS	$0.38\,\Delta T$
Ni	In glass [9]	$0.47\,\Delta T$
Ti	In ULE	$0.81\,\Delta T$
Ti	In LAS	$1.03\,\Delta T$

bination of glass and crystals. The degree of crystallinity can be controlled by heat treatment in the 700 to 1000°C range [6, 7]. The choice of metal dispersoid to give zero CTE falls first on Super Invar. This permits minimization of $(\alpha_d - \alpha_m)$ in Eq. (1), which in turn minimizes microcracking. Even though the volume fraction to give zero CTE is lower for aluminum, the effect on thermal conductivity should be increased by an order of magnitude. A compromise for thermal cycling stability would be to use titanium, which is likely to give an adherent, low-CTE, oxide interface.

Using an expression derived by Selsing [8] for the radial stresses perpendicular to the dispersoid/matrix interface, we may compare promising systems. If P is the hydrostatic pressure, R the dispersoid radius, and r the radial distance from its center,

$$-\sigma_r = P(R/r)^3 = (\alpha_m - \alpha_d)\,\Delta T\left[\frac{1+\nu_m}{2E_m} + \frac{1-2\nu_d}{E_d}\right]^{-1}\left(\frac{R}{r}\right)^3 \qquad (2)$$

It is seen that if $\alpha_d > \alpha_m$, σ_r is tensile on cooling and σ_r is maximum at $r \leqslant R$. Table I lists properties of candidate materials, while Table II summarizes calculated values of σ_r, including reported data for glass matrix systems [8, 9]. It is seen that differences in CTE require that the fabrication temperature (and hence ΔT) be minimized for Ti/LAS composites.

2. FABRICATION STUDIES

Small particle/grain/dispersoid sizes are preferred to minimize microcracking and achieve CTE uniformity. On the other hand, the most negative CTE is achievable only with a high degree of matrix crystallinity. Results of early studies in which constituent powders (Li_2O or Li_2CO_3, Al_2O_3, and SiO_2) were used indicated that the temperature required to give complete reaction to a uniform β-eucryptite also resulted in excessive lithium oxide loss and large grain sizes. A major improvement was achieved with a relatively new ceramic forming method called the sol gel process. This technique not only provided a homogeneous composition but also a method for controlling the degree of crystallinity by heat treatment of the initial glassy state.

The sol gel process was used to produce starting powders for both hot-pressing and cold-pressing and sintering. It involves mixing organometallics—lithium methoxide dissolved in methanol, aluminum isopropoxide dissolved in toluene and liquid tetraethoxy silane—refluxing for 1 h at 80°C, adding water to control the carbon constituent, evaporating at 80°C to dryness, and firing in air for 18 h at 700 to 1000°C in an alumina crucible. Above 800°C, over 80% crystallinity is expected for this time period [7]. The powder was fired at only 700°C so that the composite could be subsequently heat-treated (to fine-tune the CTE) by controlling the ratio of crystal/glass phases. X-ray diffraction analyses with nickel-filtered copper radiation and a General Electric XRD-5 X-ray diffractometer (and aDebye–Scherrer powder camera) revealed that the material calcined at 700°C did not produce an X-ray diffraction pattern. This indicated that the material was still either amorphous or consisted of extremely small crystallites (<50 Å). X-ray peaks from powder calcined at 1000°C gave excellent agreement with published diffraction data for β-eucryptite.

Compounds fabricated included β-eucryptite ($Li_2O \cdot Al_2O_3 \cdot 2SiO_2$), β-spodumene ($Li_2O \cdot Al_2O_3 \cdot 4SiO_2$), and petalite ($LiO_2 \cdot Al_2O_3 \cdot 8SiO_2$). All of these have negative volumetric CTE values for most of the temperature range of interest when they are in the crystalline form. The CTE is slightly positive when they are amorphous. Ground ULE glass with a slightly negative CTE was also studied as a matrix material. ULE is a trade name of Corning Glass Co. standing for ultralow expansion; the glass consists of SiO_2 with about 7% TiO_2. The metallic phases of dispersoids chosen for study were titanium (the Ti–6Al–4V alloy) and Super Invar (Fe–30Ni–6Co). Hot-pressing can achieve greater than 95% theoretical density at $T < 1000$°C *in vacuo* at about 35-MPa pressure. Graphite dies and plungers coated with a thin film of BN were used. A drawback of hot-pressing, however, is that densification is poor below the minimum crystallization temperature (~ 700°C). It is important to achieve adequate strength with significant control over the ratio of crystalline to amorphous phases. On the other hand, a large grain size is undesirable due to increased susceptibility to microcracking and decrease in polishability. Consequently, work was undertaken to study the feasibility of cold-pressing sol gel powders (at ~ 69 MPa) followed by sintering in the 700 to

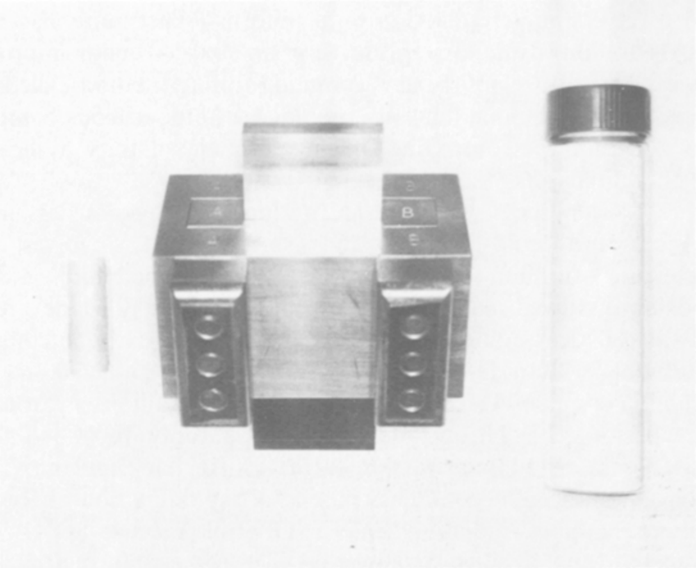

Fig. 2. From left to right: (A) unsintered cold-pressed sample, (B) cold-pressing die, and (C) jar of sol gel powder. The plunger for the tapered die cavity is seen in position on top of the die.

1000°C region. It was found that 5 vol% of a binder (microgranular cellulose powder used for column chromatography) was needed to give adequate cold strength prior to sintering. Figure 2 shows a specially constructed cold-press die for use in making shapes directly suitable for CTE tests. The die cavity is slightly tapered to facilitate the ejection of the specimen as well as the release of trapped air during the pressing, resulting in greater density and strength of the unsintered sample. An advantage of the cold-press technique is that a large number of samples can be made in a short time, and the effects of sintering temperature, time, composition, and CTE can be systematically studied.

3. THERMAL EXPANSION MEASUREMENTS

CTE measurements were performed by two methods: laser interferometry and differential dilatometry. In the double-Michelson laser interferometer [10] developed for the measurement of near-zero CTEs, two interferometers combine in reflecting beams off the polished end faces of small samples supported on a ULE glass plate. A phase locked loop tracking system was added to maintain adequate signal outputs after

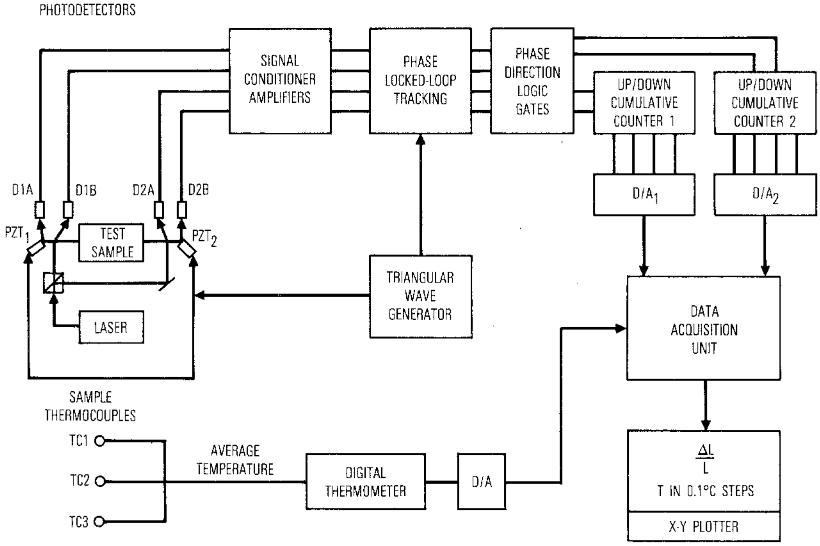

Fig. 3. Schematic of double-Michelson interferometer system showing signal processing scheme of the four photodetector signals.

spurious voltage spikes, mechanical shocks, or excessive sample movement. If phase information is lost by the photodetectors (see Fig. 3), the locked loop system compares the prior phase information with that of the piezoelectric transducer (PZT) modulation signal until the signal is restored. A microprocessor-based signal processing system enables the four photodetector signals to be converted directly $\Delta L/L$ versus temperature information.

The double-Michelson system, while providing the best available resolution and accuracy ($\Delta L/L$ to 10^{-8}), is still time-consuming to set up. Experience with linear variable differential transducers (LVDTs) suggested that available signal processing methods might obtain a length resolution of 3μin. A differential dilatometer based on an all ULE-glass system was constructed and used to provide screening results more rapidly (Fig. 4). In the region of 20–200°C, the CTE of the ULE itself is of the order of $\pm 5 \times 10^{-8}$ °C^{-1}, so that materials with CTEs of greater than 10^{-7} °C^{-1} could be readily tested. Figure 4 shows the relative positions of two LVDTs (mounted on vertical micrometer stages), ULE extension rods, and an aluminum-wrapped resistance heater tape. The sample is mounted on a ULE disk sitting on a ULE pedestal. The ULE extension rods follow the motions of the disk and the sample. A thermocouple is mounted just below the disk. Calibrations with an NBS silica standard showed that corrections were required only on heating. A Hewlett-Packard Co. HP-IL micro-

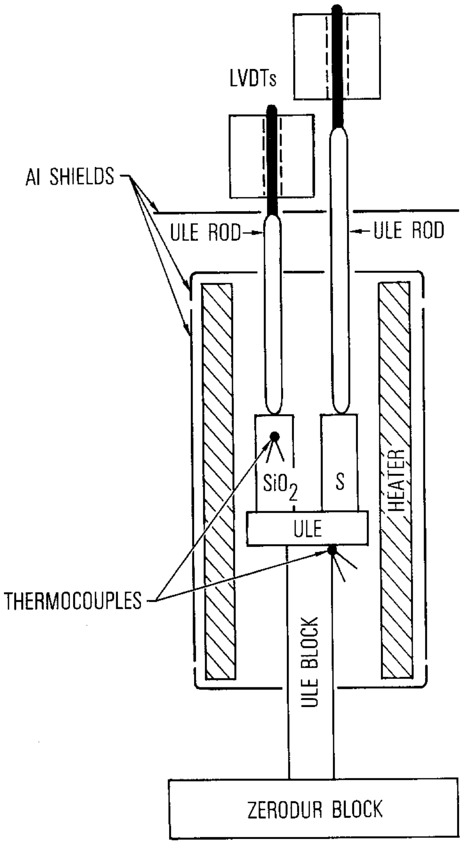

Fig. 4. Schematic of an ultralow-expansion (ULE) glass differential dilatometer. Micrometer stages are used to keep the LVDTs in their linear response ranges.

processor system takes continuous readings about 20 apart. Figure 5 shows typical results with this dilatometer for a ULE–titanium composite. Tests can be performed with this system at the rate of two samples a day. The combined capability of a differential dilatometer with a laser interferometer has proved itself invaluable in a materials development effort of this type.

4. RESULTS

Results are summarized on the basis of the four combinations of materials (β-eucryptite and ULE matrices with Ti and Super Invar dispersoids). β-Eucryptite gave a range of CTE values depending on the time and

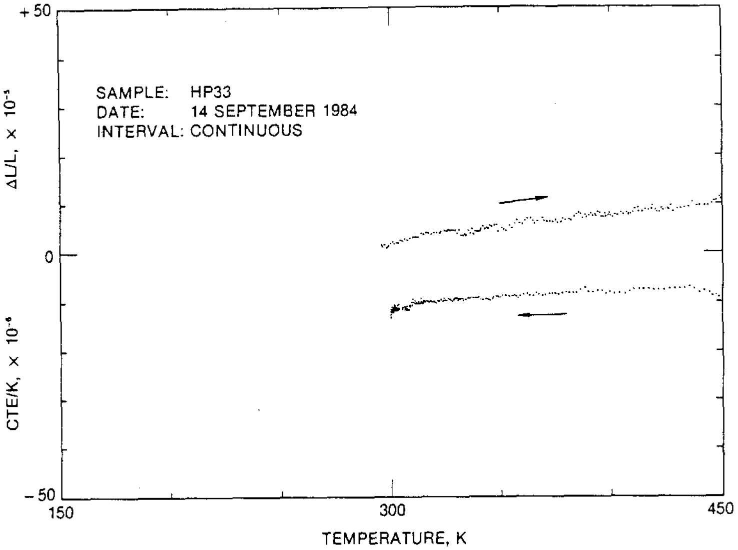

Fig. 5. ULE differential dilatometer data for a sample of ULE with 15 vol% titanium. Data points are recorded continuously at about 20-s intervals.

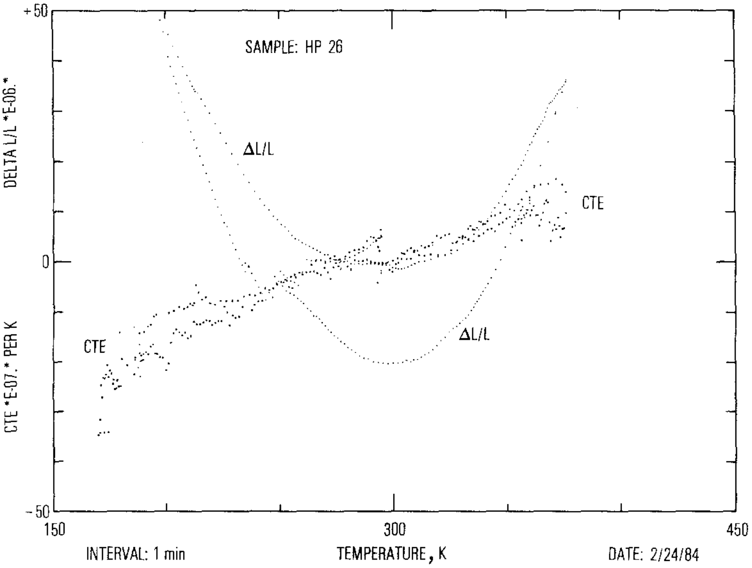

Fig. 6. Thermal strain and CTE data for a sample of β-eucryptite with 30 vol% titanium as recorded by the system shown in Fig. 3. Hot-pressed at 900°C.

temperature of heat treatment and fabrication steps. In general, more negative CTEs (to $-4 \times 10^{-6}\,^{\circ}C^{-1}$) were obtained with increased hot-pressing or sintering temperatures in the range 700 to 1200°C. With the lower fabrication temperatures there was also a tendency for the $\Delta L/L$ vs temperature curve to be U-shaped, leading to a slightly positive CTE above room temperature. The addition of titanium to β-eucryptite accentuated this tendency. Figure 6, obtained with the double Michelson, shows both the U-shape and a slight hysteresis in the $\Delta L/L$ curve. The instantaneous CTE is seen to range from about $-30 \times 10^{-7}\,^{\circ}C^{-1}$ at $-100^{\circ}C$ to about $10 \times 10^{-7}\,^{\circ}C^{-1}$ at $+100^{\circ}C$. The temperature for the reversal of the $\Delta L/L$ curve (zero CTE) shifts with the titanium content as shown in Fig. 7. An average CTE of zero can therefore be achieved by modifying the titanium content if the temperature range is specified. The titanium particles were fairly large in these samples, but little surface reaction or microcracking is obtained after thermal cycling. Smaller particle sizes and better dispersion have since been obtained. A further development should be the incorporation of a metallic phase by purely sol gel methods, so that ceramic and metallic particle sizes are equal (for optimum polishability).

Work with β-spodumene gave qualitatively similar results to that with β-eucryptite. Hot-pressing of these compositions to higher temperatures gave complex results, with CTEs ranging from -1.3 to $+3 \times 10^{-6}\,^{\circ}C^{-1}$.

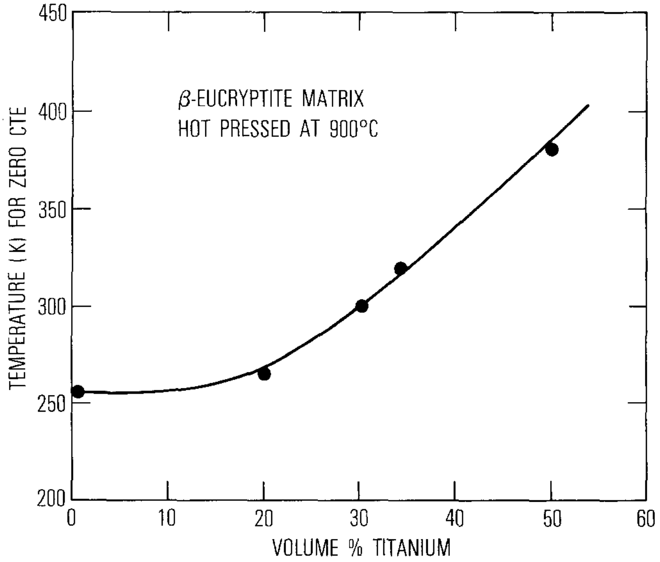

Fig. 7. Temperature for thermal strain sign reversal for β-eucryptite with varying amounts of a titanium dispersoid.

Very low CTEs over larger temperature ranges can be achieved with hot-pressed ULE matrices and titanium additions, as Fig. 5 indicates. The hot-pressed ULE powder by itself shows a slightly negative CTE.

Results were also obtained on ULE and β-eucryptite matrices with Super Invar powder additions. Super Invar (Fe–30Ni–6Co) has a near-zero CTE unless it is cooled below about 0°C, where the gamma-to-alpha phase transition takes place. The subsequent CTE ($3 \times 10^{-6}\ {}^\circ\mathrm{C}^{-1}$) [2] is still so low that substantial amounts (over 30 vol%) are needed to raise the CTE of β-eucryptite to near-zero (after hot-pressing at or above 900°C). The data point for 15 vol% Super Invar (○) in Fig. 1 shows a good agreement with prediction. A composite of ULE with 20 vol% Super Invar has a CTE of about $1.5 \times 10^{-6}\ {}^\circ\mathrm{C}^{-1}$, and a lesser amount is needed to change the slightly regative CTE of ULE to zero composite CTE.

5. CONCLUSIONS

Our results are consistent with prior work and help to define the compositional limits for achieving zero CTEs. Our data are combined with reported results in Fig. 8, which summarizes the various options available for mixing positive- and negative-type CTE materials. The objective is to

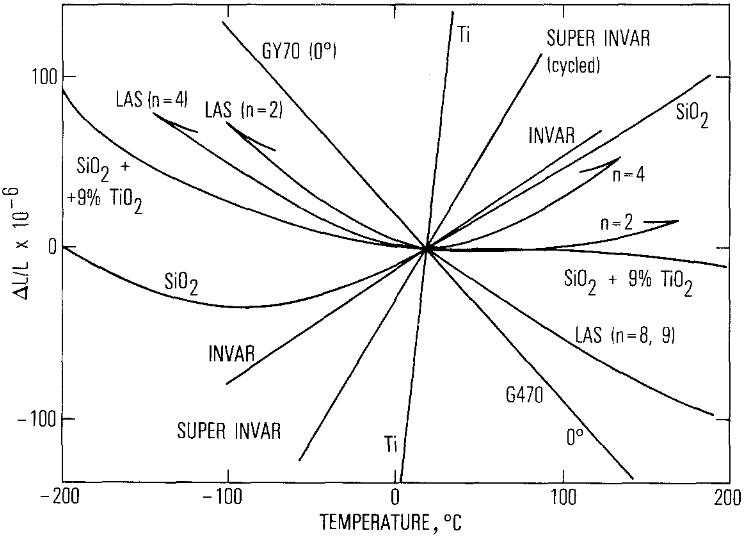

Fig. 8. Thermal microstrain versus temperature for various low-CTE materials. LAS refers to lithia–alumina–silica compounds with varying silica-to-lithia molar ratios (n). All materials are isotropic except the GY70 fiber whose axial characteristics are shown.

have materials available to provide both types over the entire temperature range of interest. Our work indicated that negative CTEs above room temperature are more difficult to obtain in the LAS system. Two exceptions appear to be β-eucryptite hot-pressed above 1000°C and petalite-based compositions, with the molar ratio of SiO_2 to LiO_2 in the region of 8 to 9.

There is a good chance of obtaining an average CTE of zero over a wide range of temperatures in the region 150 to 450 K or, at least, a CTE in the range of 10^{-10} to $10^{-8}\,K^{-1}$, the limit of measuring capability. Further work is suggested to fabricate composites with equal grain or particle sizes for optimum polishability and CTE uniformity.

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