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Thermal conductivity and specific heat of glass ceramics

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The effect of crystallization on the lattice vibrations of two glass ceramics, a magnesium aluminosilicate (Corning Code 9606) and a lithium aluminosilicate (Corning Code 9623), is studied through measurements of the thermal conductivity and specific heat below 300 K. Because of grain boundaries and magnetic impurities, measurements below a few kelvins are of limited value. At higher temperatures, however, the experimental results show that the lattice vibrations of one of the glass ceramics (Code 9606) change from glassy to crystalline upon crystallization. Those of Code 9623, however, remain glassy even in the fully crystallized state. In contrast to the crystalline Code 9606 sample, the Code 9623 sample accommodates large concentrations of interstitial lithium and magnesium ions in its crystal lattice, and it is suggested that the glasslike lattice vibrations in the Code 9623 sample are caused by these ions.

I. INTRODUCTION

In perfect crystalline solids the lattice vibrations can be described as traveling waves. All amorphous solids, however, have additional, low-energy excitations dominating the specific heat below a few kelvins. Below 1 K the specific heat approaches a linear variation with temperature. The excitations associated with this specific heat are commonly referred to as tunneling states or two-level systems (TLS's), and are believed to lead to the characteristic thermal conductivity varying as the square of the temperature.[1] Another universal feature of amorphous solids is that at high temperature their thermal conductivity increases with increasing temperature and approaches a nearly temperature-independent value near the softening temperature. Above ~50 K the phonon mean free path becomes so short that the lattice vibrations are more appropriately described as those of highly damped Einstein oscillators vibrating with random phases.[2] It is unknown what connection, if any, exists between these two apparently universal features occurring at these widely different frequencies. However, a study of this question is not the purpose of the present investigation.

While there is little doubt that all amorphous solids share these properties, there has been to our knowledge no successful demonstration that any such solid, upon recrystallization, loses both of these properties and reverts to the vibrational behavior of a crystal.[3] The failure of an early attempt[4,5] to observe a decrease of the low-temperature linear specific-heat anomaly upon recrystallization was shown to be caused by magnetic impurities which dominated the specific heat in the commercial lithium aluminosilicate glass ceramic studied (Corning Code 9623, to be described below). Subsequent specific-heat measurements on several Li_2O-Al_2O_3-$n SiO_2$ ($n > 4$) glasses and glass ceramics by Bohn[6] were also inconclusive. The interpretation of these data was difficult because of the narrow temperature range used (1.5–6.0 K); also, magnetic impurities could not be excluded. Jeapes *et al.*[7] and Leadbetter *et al.*[8] also found the linear specific-heat anomaly in amorphous GeO_2, in amorphous diopside ($CaMgSi_2O_6$), and in another lithium aluminosilicate glass ceramic ("Cer-Vit") to remain practically unchanged upon crystallization, although the lowest temperature of their measurement, 1.4 K, also precluded a convincing identification of the low-temperature anomalies. They argued, however, that magnetic impurities could be excluded in all of their samples and suggested loosely bound atoms at the grain surfaces or other localized defect states to be the cause of the specific-heat anomalies in the recrystallized samples. Without questioning the validity of these results, it must be recognized that the magnitude of the low-temperature linear specific-heat anomaly investigated is rather small. Therefore, it is not easily distinguished from other anomalies, caused, for example, by accidental impurities, especially if the measurements are not carried to temperatures well below 1 K. The low-temperature thermal conductivity, on the other hand, which is very sensitive to the anomalous glassy excitations at low temperatures (it varies as T^2 in all amorphous solids below 1 K), cannot be relied upon in recrystallized glasses to identify these low-energy tunneling states either, because of the predominance of grain boundaries as phonon scatterers, as also noted by Stephens.[4] However, as we mentioned above, the characteristic vibrational properties of amorphous solids are not restricted to low frequencies and thus, to observation at low temperatures, and we will show in this paper how measurements up to room temperature and above can be used to distinguish between glasslike and crystal-like high-frequency lattice vibrations. To anticipate the results: we will compare two commercial glass ceramics, one a lithium the other one a magnesium aluminosilicate, and will show that upon crystallization the latter will indeed behave like a crystal, while the former remains unchanged and glasslike. In the paper following this one, low-temperature internal friction measurements will be used to confirm the same conclusion through a study of the low-energy tunneling excitation in these glass ceramics.[9] Since both of these glass ceramics are chemically and physically highly disordered, these measurements will show that it takes a very special kind of disorder to lead to glasslike behavior in crystals.

II. EXPERIMENT

A. Samples

The samples studied were commercial glass ceramics ("Pyroceram") based on SiO_2 and Al_2O_3, produced by the Corning Glass Works under the Code No. 9606 and 9623, respectively; they were kindly supplied by Dr. G. H. Beall from Corning. Although the Code numbers usually refer to the crystallized ceramics, we will use the numbers here to identify the samples regardless of their state of ceramming ("ceramming" being the technical term used to describe the thermal process by which a glass article is converted to a predominantly crystalline one[10]). These glass ceramics have been described in several recent reviews[10–13] and also in the monograph by McMillan.[14]

The Corning Code 9606 is a magnesium aluminosilicate of the composition[12] (all in wt. %): SiO_2, 56.1; Al_2O, 19.8; MgO, 14.7; CaO, 0.1; TiO_2, 8.9; As_2O_3, 0.3; and Fe_2O_3, 0.1. Heat treatment of the glass for 2 h at 800 °C leads to nucleation centers ($MgTi_2O_5$) in the amorphous matrix, at 900 °C to a β-quartz solid solution, at 1010 °C to α-quartz and various other minor crystal phases, and at 1260 °C to cordierite as the dominant crystal phase ($\sim 80\%$), and also to cristobalite ($\sim 12\%$), and $MgTi_2O_5$, and rutile ($\sim 10\%$).[11] The commercially available Corning Code 9606 glass ceramic has been heat treated at 1260 °C for 8 h; we call it "fully cerammed." Grain sizes in the fully cerammed samples are in the 1–3-μm range (Ref. 11, Fig. 5). The samples we received from Corning were clear; they had been heat treated for 2 at 820 °C, and thus should still have been amorphous, with microcrystalline inclusions. We also received fully cerammed 9606 glass ceramic, which was white. The thermal diffusivity above room temperature after intermediate stages of crystallization has been reported previously.[15]

The other glass ceramic studied, Corning Code 9623, is a member of the TiO_2 and ZrO_2 nucleated lithium aluminosilicate family, which are widely used commercially, e.g., as Corning's "Vision" transparent cookware (Code 9607) and Schott's "Zerodur" (for their exact compositions, see Ref. 12, Table I), and as "Cer-Vit" produced by Owens-Illinois. Our piece of 9623 had been cut from a mirror blank. Its chemical composition is that given in Ref. 13, Table I), as composition 1 (in wt %): SiO_2, 65.0; Al_2O_3, 23.0; MgO, 1.8; Li_2O, 3.8; ZnO, 1.5; As_2O_3, 0.9; ZrO_2, 2.0; and TiO_2, 2.0 (this composition is close to that of Corning's "Vision"). As received, our sample had already been heat treated through three steps of the ceramming process: The glass had been melted at 1650 °C and then quenched. Heat treatment at around 725 °C had produced amorphous phase separation. Further heat treatment at around 800 °C had led to a $ZrTiO_4$ nucleating phase. Continued treatment at this temperature had caused a silica-based crystal phase to grow from these precipitated nuclei. This hexagonal phase has been designated as a stuffed β-quartz solid solution where Li, Al, Mg, Zn, and As are the solutes in the SiO_2 crystal. The third stage of the heat treatment, at around 900 °C, produced a sample with $\sim 95\%$ crystallinity (as determined by x-ray diffractometer measurements) and crystallites smaller than 0.1 μm. The sample (which was received from Corning in this form) was amber in color and transparent. Scanning electron microscopy of a fracture surface could not resolve the microstructure, but dark-field transmission microscopic examination of the material indicated a mean crystallite size of 600 Å.[5] An x-ray-diffraction pattern for this sample showed the lines characteristic for β-quartz solid solution. Additional heat treatment at 900 °C for 8 h changed neither the crystallite size nor crystal structure. Heat treatment at higher temperatures ($T > 950$ °C) is known to cause this material to transform to the tetragonal β-spodumene (keatite) solid-solution structure and also induces crystallite growth. One set of samples was heated *in vacuo* in a silica breaker at 1080 °C for 1 h.[16] The second set of samples was heated *in vacuo* for 1 h at 1175 °C. The heating and cooling rates were 600 °C/h. The samples heated at 1080 °C were almost completely opaque, but retained slight translucency. The samples treated at 1175 °C were completely opaque. As predicted, heat treatment of the as-received material at $T = 1080$ °C produced a crystal phase transformation to the β-spodumene structure, as revealed by x-ray-diffraction samples. Heat treatment at $T = 1175$ °C produced the same crystal structure as heat treatment at $T = 1080$ °C. Scanning micrographs of the two heat-treated samples of Code 9623 showed microstructure of the 1080 °C specimen on a scale of 0.3–0.5 μm, while that for the 1175 °C was on the scale of 1–2 μ. This microstructure is comparable to that seen on similar materials.[12].

Because of their chemical composition and also because of the complexity of their crystal structures, we expect the crystallites in these glass ceramics to be chemically and physically highly disordered. However, both the fully cerammed 9606 and heat-treated 9623 (1175 °C for 1 h) contain no more than approximately 5% amorphous material. In the 9606 this is concentrated in the nodes between the crystalline grains; in glass ceramics such as the 9623 it is also located along the grain boundaries [G. H. Beall (private communication)]. This residual glass should have no noticeable effect on our measurements.

When we originally reported the work presented in the following [J. R. Olson, D. G. Cahill, H. E. Fischer, R. O. Pohl, Bull. Am. Phys. Soc. **35**, 547 (1990)], we erroneously misnamed the Code 9623, calling it Code 9608. The latter is a very common glass ceramic ("Corningware," composition in Ref. 12, Table II), but only has TiO_2 to initiate the nucleation and very little ZrO_2.

B. Thermal conductivity

Thermal conductivity was measured with the standard steady-state technique (abbreviated as dc in the following) using various cryostats to cover the temperature range from 0.05 to 100 K. Between 30 and 300 K, both an ac diffusive heat-wave technique[17] abbreviated as 3ω) and a diffusive heat-pulse technique[18] (abbreviated as HP) were used. The extension of the measurement on fully cerammed 9606 to 700 K was done with the 3ω technique. For the present work, the HP technique has been modified by interfacing the data-acquisition system to an IBM PC-AT computer. The computer directs hardware, which controls the temperature, sends the necessary square heat pulse to the sample heater, measures the temperature on the opposite side of the sample, and analyzes the data. Details are described elsewhere.[19]

For the dc measurements, rod-shaped samples several centimeters in length and a few millimeters in diameter were used. Heater and thermometers were attached to metal clamps fastened to the samples. Alternatively, a copper foil was attached to one end using Stycast 2850 epoxy and a 1000-Ω heater was soldered to this foil. Copper wire was twisted around the sample in two places along the length of the sample and attached with GE 7031 varnish. Carbon resistance thermometers were then attached to these copper wires. The base of the sample was mounted into a copper clamp with indium metal serving as a cushion and providing good thermal contact. For the HP measurements, the samples were cut from a rod using a diamond saw. The disks were generally 0.8 cm in diameter and 0.6 mm thick. After polishing with SiC grit, they were heat treated as described in Sec. II A. Thin metal films were evaporated onto the opposing surfaces to serve as heater and thermometer. For the 3ω technique, sample preparation followed exactly the technique described in Ref. 17. After cutting the samples to $10\times10\times1$ mm^3 with a diamond saw, a heater-thermometer film was evaporated onto one of the large faces without any further surface treatment.

C. Specific heat

The diffusive heat-pulse (HP) technique can also be used for measuring the specific heat above 30 K.[18] Below 30 K the quasiadiabatic transient heat-pulse technique was used. Between 0.1 and 20 K the sample was mounted in a dilution refrigerator; for details, see Refs. 16 and 20. Measurements between 2 and 20 K were also performed in a ^{4}He cryostat as described in Refs. 21 and 22.

D. Predictions of thermal properties using the Debye model

The longitudinal and transverse speeds of sound at 4 K of the as-received Code 9623 (0.06-μm crystallite size) have been measured by Stephens.[4] From these data and the mass density $\rho=2.42$ g cm^{-3}, he calculated the Debye speed of sound to be $v_D=4.12\times10^5$ cm s^{-1}, identical to that of a-SiO$_2$. From these values the Debye low-temperature specific heat is calculated according to

$$c_p(T)=1.237\times10^{11}T^3v_D^{-3}\rho^{-1}\ \mathrm{J\,K^{-4}\,s^{-3}}$$
$$=7.31\times10^{-7}T^3\ \mathrm{J\,g^{-1}\,K^{-4}}\ . \quad (1)$$

Using the gas-kinetic formula for the thermal conductivity, we can write

$$\Lambda(T)=\tfrac{1}{3}c_p\rho v_D\bar{l}$$
$$=4.12\times10^{10}\bar{l}T^3v_D^{-2}\ \mathrm{J\,K^{-4}\,s^{-3}}\ , \quad (2)$$

where $\bar{l}$ is an average mean free path for the Debye waves. From the given Debye speed of sound, it follows that

$$\Lambda(T)=2.43\times10^{-1}\bar{l}T^3\ \mathrm{W\,cm^{-2}\,K^{-4}}\ . \quad (3)$$

Equations (1) and (3) were used throughout this paper for comparison of the low-temperature data with the Debye model.

III. EXPERIMENTAL RESULTS

The thermal conductivities of Code 9606 in the as-received amorphous and the fully annealed states are compared with those of $a-\mathrm{SiO}_2$ and of α-quartz in Fig. 1. In the amorphous state, the thermal conductivity is almost indistinguishable from that of a-SiO$_2$, as is known for other silica-based glasses (e.g., the borosilicate Corning Code 7740, called "Pyrex"[17,23]). Upon ceramming, the thermal conductivity above ~10 K increases drastically and approaches that of single-crystal quartz near room temperature. The decrease below 100 K is caused by grain-boundary scattering; the dashed line marked $l=2\,\mu$m is the thermal conductivity calculated with Eq. (3) under the assumption that all phonons are diffusely scattered at the boundaries of grains 2 μm in diameter. The decreasing slope of the measured conductivity near 0.1 K may indicate that the grain boundaries cease to be strong phonon scatterers for the dominant phonons at these temperatures (see the dominant phonon wavelengths indicated at the top of the graph). We mention in passing that the thermal conductivity of the fully crystallized 9606 agrees with earlier measurements [1.5–4 K (Ref. 24) and $T>100$ K (Ref. 25)]. Since this material is widely used as a thermal conductivity standard, we will examine this agreement more carefully in another place (Olson, Fischer, and Pohl[15]).

The specific heat c_p of 9606 is shown in Fig. 2, where c_p/T^3 is plotted versus temperature T. The rapid increase as T decreases below ~5 K is caused by magnetic impurities which are masking the low-energy glassy excitations (see also the data for Code 9623, shown below). Thus, in this temperature range, the measurements can yield no information about glassy excitations. Above 5 K, however, c_p/T^3 shows the characteristic variation as the glass is crystallized: c_p/T^3 peaks at higher value and at a lower temperature in the amorphous than in the crystalline state, as has been observed often,[26] and is also shown in Fig. 2 for SiO$_2$, for which the change is exceptionally large (note that the increase of c_p/T^3 observed for this highly pure a-SiO$_2$ below 2 K is indeed caused by the low-energy glassy excitations).

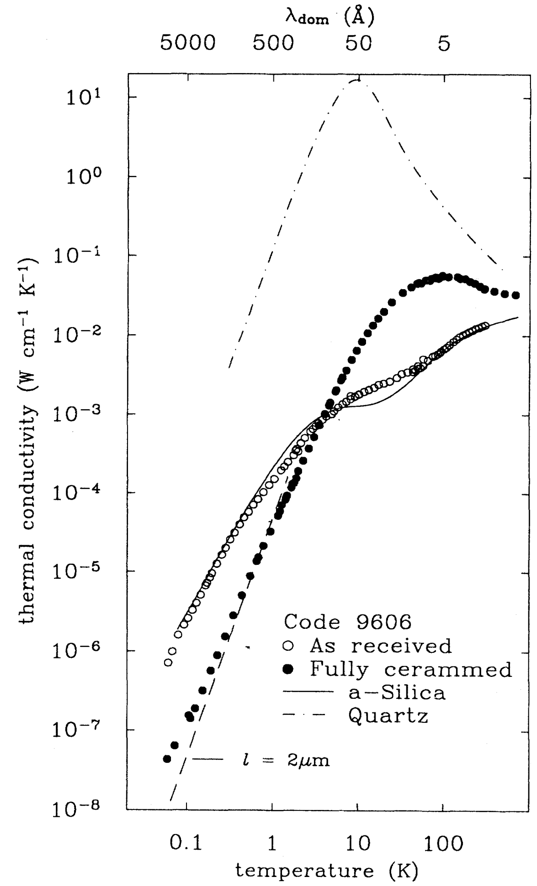

FIG. 1. Thermal conductivity of Corning Code 9606, a magnesium aluminosilicate, in the amorphous form, i.e., after 2 h at 820 °C (open circles) and in the fully crystallized (cerammed) form after subsequent heating to 1260 °C for 8 h (solid circles). Dashed line: theoretically expected thermal conductivity for a wavelength-independent phonon mean free path $l = 2$ μm, close to the average crystallite size. For comparison are shown the thermal conductivity of α-quartz (dot-dashed curve) and of a-silica (solid curve). Upper scale: dominant phonon wavelength [for a recent discussion, see Tom Klitsner and R. O. Pohl, Phys. Rev. **36**, 6651 (1987)] for a Debye velocity $v_D = 4.1 \times 10^5$ cm/s (a-SiO$_2$). That velocity is close to that of Pyroceram at 4 K (see Sec. II D).

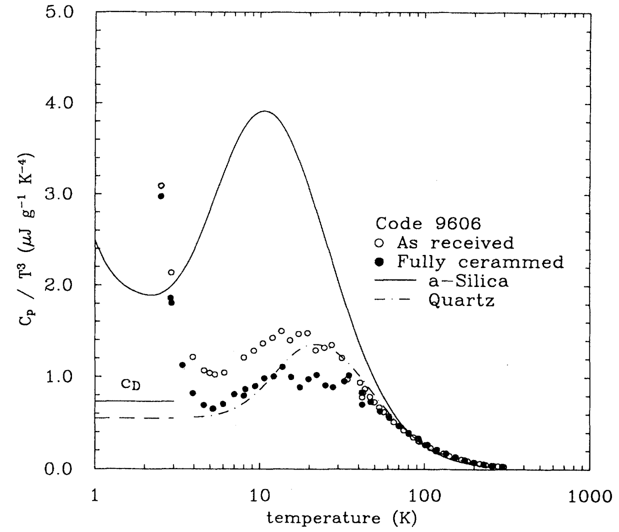

FIG. 2. Specific heat c_p divided by the temperature cubed for Code 9606 as received (Sec. II A) and fully crystallized (cerammed). The short solid line labeled c_D is the Debye specific heat (divided by T^3) for 9606 (calculated from elastic measurements, Sec. II D); the short dashed line underneath is that for quartz. The rapid rise of c_p below 5 K in 9606 is caused by magnetic impurities. c_p/T^3 for amorphous and crystalline SiO$_2$ are shown for comparison.

The response of the Code 9623 to heat treatment is remarkably different (Fig. 3). Since the as-received sample was already predominantly (~95%) crystalline (stuffed β-quartz) with grain sizes averaging 600 Å, one might have expected the thermal conductivity to be that of a microcrystalline solid, similar to that of the cerammed 9606 (Fig. 1). Instead, it is very close to that of an amorphous solid (see the comparison with a-SiO$_2$ in Fig. 3). The somewhat lower conductivity between 0.1 and 30 K can be explained with additional phonon scattering by the grain boundaries: Their influence will be noted if the phonon wavelength is comparable to or smaller than the grain size (since longer-wavelength phonons will average over several grains) and if any scattering processes other than grain-boundary scattering lead to mean free paths larger than the grain size. These two conditions are met between 0.1 and 30 K, as can be seen by inspecting the scale of the dominant phonon wavelengths shown at the top of Fig. 3 and by a comparison with the average phonon mean free path determined[23] for a-SiO$_2$, which has a very similar speed of sound. This mean free path is 500 Å at 10 K, dropping to 20 Å at 30 K.

It is not surprising that an 8-h heat treatment at 900 °C does not change the thermal conductivity of this sample (Fig. 3), since neither crystallite size nor crystal structure were found to change. However, even the high-temperature treatment at 1175 °C, which led to the formation of large crystallites of a different crystal structure (stuffed β-spodumene solid solution), only causes a change in grain-boundary scattering, observed below 30 K in Fig. 3, without affecting the glasslike thermal conductivity within the grains ($T > 30$ K). How little the conductivity changes in this latter temperature range is shown in Fig. 4, where we have plotted the ratio of the thermal conductivity of the 1175 °C heat-treated sample (smooth spline fit) divided by that of the as-received 9623. Between ~30 and 300 K, this ratio varies by less than 10% (the rise below 30 K is caused by the change in grain-boundary scattering; compare with the dashed line in Fig. 3, which shows the conductivity predicted at low temperatures for a ceramic with 1-μm grain size).

Without any doubt the thermal conductivity of fully amorphous 9623 (which was not measured) would have been very close to that of a-SiO$_2$, as are all silica-based glasses (e.g., Ref. 17). Our measurements have shown that ceramming the 9623 does not change the glasslike

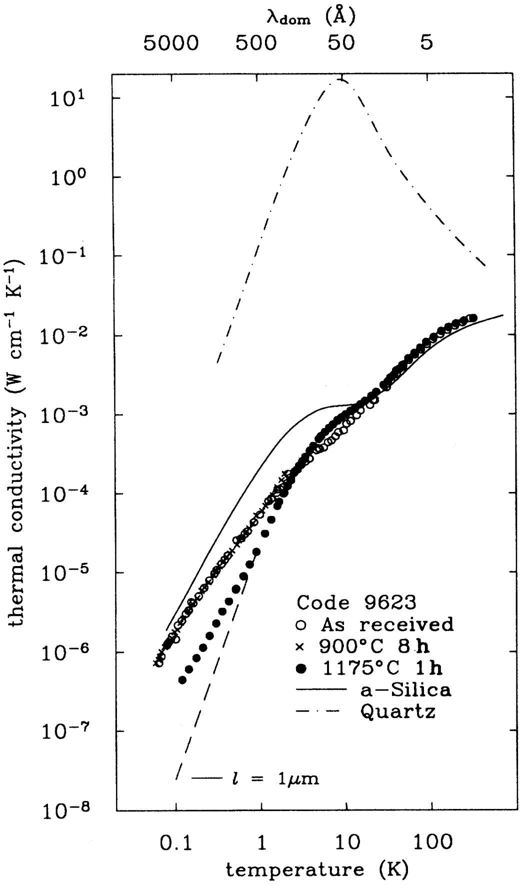

FIG. 3. Thermal conductivity for Code 9623, as received (open circles) and after heating at 900 °C for 8 h (X's) and at 1175 °C for 1 h (solid circles). Dashed line: thermal conductivity for a phonon wavelength-independent mean free path $l = 1$ μm (=average grain size in the 9623 after 1 at 1175 °C). Conductivity for amorphous and crystalline SiO$_2$ are shown for comparison.

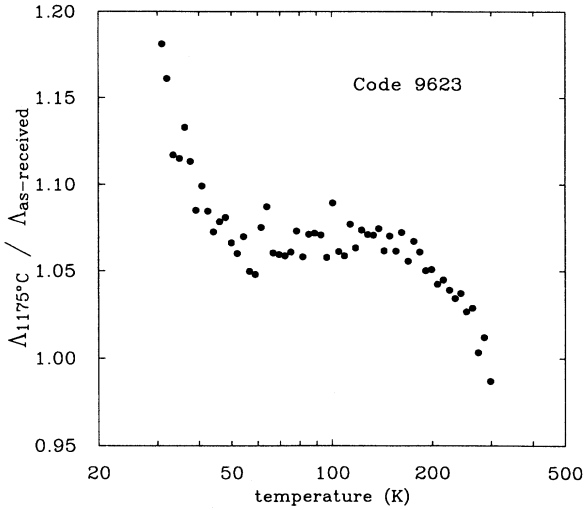

FIG. 4. Ratio of the thermal conductivity of the glass ceramic 9623 heat treated for 1 h at 1175 ° C (called $\Lambda_{1175\,°C}$) to that of the as-received one. Note the very small variation between ~30 and 300 K.

thermal conductivity; it only leads to additional grain-boundary scattering. [Note that another microcrystalline glass ceramic of similar composition ("Zerodur," manufactured by Schott, composition given in Ref. 11, grain size 500 Å), has been found to have a very similar thermal conductivity between 2 and 300 K (Ref. 27).]

The specific heat c_p of 9623 also behaves much more like that of a glass than of a crystal (see Fig. 5). The specific heat of the as-received microcrystalline sample is even closer to that of vitreous silica than that of the amorphous as-received 9606 sample, shown in Fig. 2 as $c_p T^{-3}$. Further heat treatment (1 h at 1175 °C) increases the specific heat of 9623 around 15 K very slightly, rather than decrease it, as one would have expected. (A similar behavior was found in another lithium aluminosilicate glass ceramic, "Cer-Vit."[8] Its specific heat increased when the glass was heat treated to become a microcrystalline stuffed β-quartz solid solution of grain size ≤ 0.1 μm.) We also measured the Code 9623 after a 1-h heat treatment at 1080 °C and found a specific heat intermediate between two curves shown in Fig. 5. While the low-temperature measurements (<5 K) in Fig. 5 are meaningless because of the magnetic impurities (they have been studied in a magnetic field by Stephens[4]), the measurements above this temperature confirm the conclusion reached in thermal-conductivity measurements, i.e., that this crystalline material continues to have the lattice vibrations of a glass.

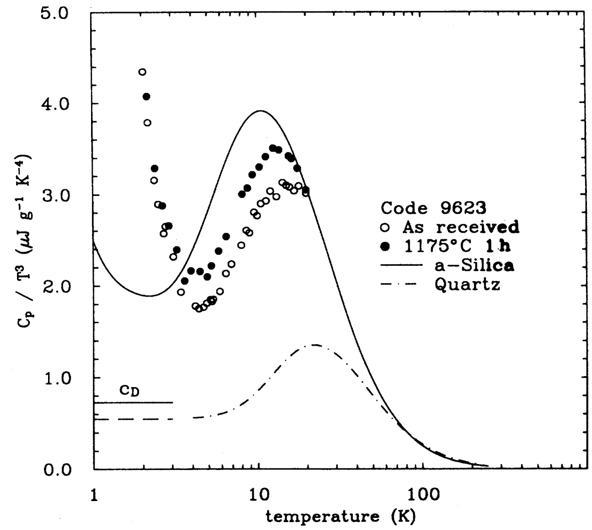

FIG. 5. Specific heat c_p divided by T^3 for Code 9623 as received and heat treated at 1175 °C for 1 h. The specific heat for the sample heat treated for 1 h at 1080 °C is intermediate between that of the as-received and the 1175 °C, 1-h heat-treated sample and has been omitted for clarity. Amorphous and crystalline SiO$_2$ are shown for comparison. The short lines marked c_D are the Debye specific heats for 9606 (solid curve), believed to be close to that of 9623, and for quartz (dashed curve), respectively (divided by T^3).

IV. DISCUSSION

The measurements presented here have shown that by extending the measuring temperature above that of the standard low-temperature range—in the case of the thermal conductivity to as high as 300 K or higher—an identification of the lattice vibrations of these two glass ceramics can be achieved. The 9606 behaves as we would expect: crystallization of the glass leads to the lattice vibrations of a crystal. It is, in fact, the only amorphous solid for which this change has been demonstrated to date. However, this straightforward and expected result arrives together with a complication: The crystalline 9623 remains entirely glasslike upon crystallization. Both ceramics are chemically and structurally highly complex solids. What causes them to behave so differently?

Before searching for potential structural causes, let us briefly review some disordered crystals in which glasslike lattice vibrations have been previously identified through measurements of their thermal properties.[28]

Zr:Nb (20 at. %).[29] In this alloy two phases, the ω and β phases, coexist. It has been suggested that small atomic motions lead to fluctuations between these phases and thus to the low-energy excitations.

ZrO_2*:*Y_2O_3.[30] Substitutional incorporation of yttrium ions leads to vacancies on the oxygen sublattice. This leads to large local strain fields.

The so-called dirty ferroelectrics.[31] In these mixed ferroelectrics, large vacancy concentrations can occur.

Alkali-halide–cyanide mixed crystals.[32] The CN^- ions lead to random local strains. It has been suggested[33] that these strains will allow a small concentration of the CN^- to retain their orientationaly mobility, thus leading to low-energy (tunneling) states.

$Ar_{1-x}(N_2)_x$.[34] Experimentally, a similar situation as in the alkali-halide mixed crystals. In the quadrupole glass state, a linear specific heat has been observed, and the thermal conductivity also shows similarities to those of amorphous solids. Again, the randomly oriented N_2 molecules are expected to lead to local strains.

YB_{66}.[35] The yttrium ions are randomly arranged over twice their number of interstitial sites.

$Ba_{1-x}La_xF_{2+x}$.[36] Substitution of La^{3+} for Ba^{2+} leads to large concentration of interstitial F^-.

Feldspars.[37] In this framework aluminosilicates Al^{3+} can occupy a Si^{4+} site. To preserve neutrality, alkali (Na^+,K^+) or alkaline earth (Ba^{2+}) ions are introduced on interstitial sites. Glasslike behavior is often, though not always, observed, even in highly perfect single crystals.

Even if we consider only the nominal ingredients of the two glass ceramics studied here, their compositions are highly complex. Nonetheless, one can identify one structural difference which may explain their different thermal behavior: Both are aluminosilicates, in which charge balance is achieved predominantly by Mg^{2+} in the 9606 and by Li^+ and by Mg^{2+} in the 9623. In the major crystalline constituent of 9606, cordierite, the Mg^{2+} ions occupy a regular array of lattice sites.[38] The 9623 sample was already almost fully crystallized when we received it. Its predominant crystal phase was a stuffed β-quartz solid solution, i.e., a framework structure in which the SiO_4 and AlO_2 tetrahedra are arranges as in the high-temperature β phase of SiO_2, with the lithium or magnesium ions, which are required for neutrality, stuffed into interstitial sites. Further heating leads to a β-spodumene solid solution. This structure is a polymorph of the SiO_2 phase keatite, again with interstitial Li^+ and Mg^{2+} for neutrality. In stoichiometric β-spodumene (Li_2O-$Al_2O_3nSiO_2$, with $n=4$), the four Li^+ ions in the unit cell occupy randomly one-half of the interstitial sites available to them in this aluminosilicate framework.[39] In the β-spodumene solid solution (i.e., $n>4$, with $n\sim6$ in 9623), the fraction of filled interstitial sites will be somewhat smaller; some of the Li^+ will also be replaced by Mg^{2+}. We are, therefore, dealing with a random array of interstitial ions, somewhat similar to the situation in the feldspars or in $Ba_{1-x}La_xF_{2+x}$ or YB_{66}, in which crystal's glasslike behavior has been observed. We therefore suggest that it is the presence of the interstitial ions in the 9623 that leads to the glasslike behavior in the crystallized form. In the 9606, in which interstitial ions do not form part of the structure, crystalline behavior is observed, regardless of any other disorder which we expect to exist in both types of glass ceramics. In the following paper,[9] the same conclusion will be reached in a study of the low-energy excitation in these glass ceramics. These findings lend further support to the suggestion that large concentrations of local distortions in crystal lattices, as caused, for instance, by a random arrangement of interstitial ions, can lead to vibrational properties similar to those of amorphous solids.[40]

[Earlier in the paper, we had referred to measurements on two other glass ceramics, Cer-Vit[7] (low-temperature specific heat) and Zerodur[27] (thermal conductivity). They are also both lithium aluminosilicates, crystallizing in the same way as the 9623. Thus it is not surprising that these glass ceramics showed glasslike behavior at all stages of crystallization. If the Cer-Vit studied by Leadbetter *et al.*[8] was indeed free of magnetic impurities, the linear specific-heat anomaly that persisted in that sample after it had been crystallized (cerammed) may indeed have been caused by the low-energy glassy excitations in the β-quartz solid solution.]

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