

# A Critical Review of Dental Lithia-Based Glass–Ceramics

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## Abstract

The purpose of this article is to review current understanding of lithia-based glass–ceramics and to identify future research needs for this class of dental materials in relation to novel compositions and fabrication methods. With rapid advances in material development and digital technology, time efficiency of dental workflow and fit accuracy of ceramic restorations are ever improving. Lithia-based glass–ceramics are at the forefront of this advance—new variants with more efficient fabrication routes are continually being introduced into the marketplace. Base glass composition, crystallization heat treatment, nucleant and coloration additives, and property gradation are some pertinent variables. The trend in fabrication is to move from CAD/CAM grinding of partially crystallized glass–ceramics to fully crystallized materials, thereby circumventing the need for postmachining firing altogether. In these endeavors, a better understanding of mechanical properties and evolving shaping technologies, such as ductile grinding, is paramount. Additive manufacturing and 3-dimensional printing methodologies offer a promising alternative to current CAD/CAM subtractive manufacturing routes. Challenges to the implementation of new technologies in efficient development and production of high-quality dental glass–ceramic prostheses are addressed.

**Keywords:** glass composition, clinical performance, mechanical properties, graded structures, ductile grinding, additive manufacturing

## Introduction

The first practical synthetic glass–ceramic was inadvertently fabricated by S.D. Stookey of Corning Glass Work in 1954 (Fu et al. 2016). Chroniclers dwell on the series of serendipitous events that led to Stookey's discovery: the furnace overheating due to a faulty temperature controller, followed by an accidental dropping of a fired sample onto a concrete floor (Zanotto 2010). Tellingly, this first glass–ceramic material was a partially crystallized lithium disilicate glass (Fu et al. 2016). Since then, a variety of glass–ceramics has evolved at Corning and elsewhere, with uses ranging from common consumer products to high-tech electronic, optical, chemical, and mechanical devices; in applications as diverse as aerospace components and implant surgery; and of particular relevance here, to dental prostheses (James 1995; Zanotto 2010).

Glass–ceramics are inherently brittle but can be manufactured with acceptably high strengths by compositional and processing refinements. Ceramics do not approach the toughness of metals, and fractures can propagate from any defect in a ceramic prosthesis, exacerbated by moisture-assisted crack growth and mechanical fatigue in cyclic loading (Zhang et al. 2013). Restorations, as with the surrounding dentition, must survive local bite forces, which can exceed several hundred newtons in a hostile oral environment. Long-term failure from a variety of fracture modes is a persistent concern. Lithia-based compositions are compelling for their capacity to withstand reasonably high occlusal stresses while possessing outstanding aesthetic qualities.

We first survey the evolutionary history of this class of dental glass–ceramics, culminating in modern-day variants, with specific attention to the roles of glass–ceramic compositions and vital fabrication variables. Chemical and microstructural characterizations of current lithia glass–ceramics have been extensively summarized elsewhere (Lubauer et al. 2022; Phark and Duarte 2022). We then consider vital mechanical properties that govern durability—machinability, strength, toughness, and fatigue. Building on robust clinical evidence and laboratory testing, we foreshadow potential future development of next-generation glass–ceramics, including some innovative manufacturing methodologies. The virtues of lithia glass–ceramics in relation to competing dental materials, notably zirconia, are discussed.

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**Table.** Variants of Selected Commercial Dental Lithia Glass–Ceramics.

Material <sup>a</sup>	Manufacturer (Date Launched)	Crystalline Content, vol% <sup>b</sup>	E, GPa <sup>b</sup>	H, GPa <sup>c</sup>	T, MPa·m <sup>1/2</sup> <sup>b</sup>	S, MPa <sup>c</sup>
Predominantly Li <sub>2</sub> Si <sub>2</sub> O <sub>5</sub>						
IPS e.max Press	Ivoclar Vivadent AG (2005)	61	101	6.88 ± 0.39	2.25 ± 0.17	445 ± 47
IPS e.max CAD	Ivoclar Vivadent AG (2006)	70	103	6.63 ± 0.21	2.13 ± 0.10 <sup>c</sup>	462 ± 34
Initial LiSi Press	GC Corp. (11/2016)	50	103	7.22 ± 0.31	2.11 ± 0.10	475 ± 25
Initial LiSi Block	GC Corp. (9/2021)	55	96	7.02 ± 0.13	1.50 ± 0.04	396 ± 34
Amber Press	HASS Corp. (12/2020)	58	106	6.73 ± 0.09	2.29 ± 0.08	531 ± 39
Amber Mill	HASS Corp. (5/2018)	66	98	7.75 ± 0.27	1.71 ± 0.04	336 ± 70
Ambria Press	Vita Zahnfabrik (11/2021)	74	100	6.34 ± 0.10	2.31 ± 0.22	396 ± 63
CEREC Tessera	Dentsply Sirona (7/2021)	47	103	7.37 ± 0.19	1.45 ± 0.10	367 ± 57
Predominantly Li <sub>2</sub> SiO <sub>3</sub>						
Obsidian	Glidewell Laboratories (1/2013)	43	100	7.24 ± 0.22	1.84 ± 0.06	360 ± 45
Biphasic						
Li <sub>2</sub> SiO <sub>3</sub> /Li <sub>2</sub> Si <sub>2</sub> O <sub>5</sub>						
Suprinity PC	Vita Zahnfabrik (3/2013)	57	103	7.75 ± 0.05	1.39 ± 0.04	245 ± 34
Celtra Duo	Dentsply Sirona (6/2013)	51	108	7.89 ± 0.19	1.45 ± 0.08 <sup>c</sup>	210 ± 35
Celtra Press	Dentsply Sirona (8/2017)	45	106 <sup>c</sup>	7.15 ± 0.27	2.36 ± 0.20 <sup>c</sup>	624 ± 106
LiAlSi <sub>2</sub> O <sub>6</sub> /Li <sub>2</sub> Si <sub>2</sub> O <sub>5</sub>						
NICE	Institut Straumann AG (4/2017)	80	92	6.00 ± 0.20	1.53 ± 0.05	350 ± 50

Where applicable, data are shown in mean ± SD.

E, modulus; H, hardness; S, strength; T, toughness.

<sup>a</sup>All commercial lithia glass–ceramics use P<sub>2</sub>O<sub>5</sub> as a primary nucleating agent; thus, all contain a Li<sub>3</sub>PO<sub>4</sub> phase (5 to 15 vol%). All specimens were crystallized and then polished. When required, crystallization firing was carried out by using manufacturer-recommended programs for conventional furnaces. No postpolishing glaze firing was performed.

<sup>b</sup>Data from Lubauer et al. (2022).

<sup>c</sup>Data measured in our laboratories on 1-μm polished surfaces: H from Vickers tests at 10 N (n = 10); S from piston-on-3-ball biaxial flexure test with discs of 12-mm diameter and 1-mm thickness (n = 10).

## Evolution of Dental Glass–Ceramics

### Early Compositions

The first commercial glass–ceramic material used for restorative dentistry was a heat-pressable fluorosilicate material with the trade name DICOR developed by Corning Glass Works (Corning Inc.; Malament and Grossman 1987). It was a derivative of the machinable micaceous glass–ceramic MACOR developed by the same company (Grossman 1972). DICOR consists of tetrasilicic fluorine mica crystals in the form of individual sheets or flakes embedded in a glass matrix (Beall 1992). Its microstructure, analogous to a house of cards, was highlighted by easy cleavage at the crystal–glass interfaces, enabling CAD/CAM shaping. The machinable version DICOR MGC was industrially fabricated as blanks consisting of 70% mica (Li et al. 2014). DICOR was straightforward to process in a dental laboratory and possessed high chemical durability and translucency. However, this material never achieved the combination of toughness and strength needed for structural longevity, and a high fracture rate of restoration failures (Malament and Socransky 1999; Malament and Socransky 2010) ultimately led to withdrawal from the market.

The demise of DICOR left the door open for more reliable heat-pressable glass–ceramics. Enter IPS Empress, a leucite aluminosilicate material introduced in 1991 by Ivoclar Vivadent. This marked the beginning of Ivoclar's preeminence in the dental glass–ceramic market over the next 2 decades. The IPS Empress material has a CAD version, and IPS Empress CAD and Press materials remain in use today.

### Lithia-Based Glass–Ceramics

IPS Empress 2, launched in 1998 by Ivoclar Vivadent, was the first commercial lithia-based silicate glass–ceramic (Schweiger et al. 1999). It was succeeded by IPS e.max Press (Ivoclar Vivadent) in 2005; the latter showed superior aesthetic and mechanical properties (Zhang and Kelly 2017). A year later, IPS e.max CAD was introduced. The development of IPS Empress CAD and e.max CAD was significant since it propelled glass–ceramics into the chairside material market. Lithia glass–ceramics owe clinical success to their requisite mechanical and translucency properties (Lubauer et al. 2022). That success is evidenced by the sheer number of restorations currently fabricated from these materials. During an initial 8-y span (2005 to 2013), Ivoclar Vivadent delivered >75 million IPS e.max CAD and Press restorations (Goff 2014). Prompted by this proliferation, a battery of commercial lithia silicate glass–ceramic materials has since been developed by other manufacturers, starting in 2013 with Obsidian by Glidewell Laboratories in January, Suprinity PC by Vita Zahnfabrik in March, and Celtra Duo by Dentsply Sirona in June. This trend has continued throughout the past decade, with notable newcomers in CEREC Tessera by Dentsply Sirona in July 2021 and Initial LiSi Block by GC Corp. in September 2021. Current lithia-based glass–ceramics are listed in the Table, along with pertinent mechanical properties.

Broadly speaking, dental lithia silicate glass–ceramics have 3 variants: lithium disilicate (Li<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>—LDS), lithium silicate (Li<sub>2</sub>SiO<sub>3</sub>—LS), and biphasic LS/LDS or LAS/LDS (LiAlSi<sub>2</sub>O<sub>6</sub>/Li<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>). Most lithia dental glass–ceramics use P<sub>2</sub>O<sub>5</sub> as a

primary nucleating agent (Höland and Beall 2019), while some use  $ZrO_2$  as a secondary nucleant (Beall 1992). A trend in developing new lithia silicates is to diminish crystal size, while preserving  $\geq 50$  vol% crystallinity to facilitate machinability and subsequent polishing capacity.

With the current movement toward digital dentistry, speed in restoration fabrication is becoming a pressing issue. The field has now evolved from grinding partially crystallized blocks followed by crystallization and glaze firing (e.g., IPS e.max CAD, Obsidian, Suprinity PC, Amber Mill) to grinding fully crystallized blocks with only an additional postgrind glaze firing (to partially “heal” any machining defects) and finally to grinding fully crystallized materials without any postgrind heat treatment (Initial LiSi Block, N!CE). Recent effort has been devoted to speed firing for crystallization, pre-saging a ceramic-based restoration that could be machined, polished, and seated, again with no need for any postgrind firing. The financial ramifications of such efforts promise to be substantial.

## Material Science of Lithia Glass–Ceramics

### Composition and Microstructure

All glass–ceramics require some form of crystallization heat treatment. However, compositional and microstructural evolution during crystallization of various lithia-based glasses is not fully understood. An illustrative way to unveil these elusive and often complex reaction pathways is by in situ x-ray thermodiffraction in conjunction with scanning electron thermomicroscopy and differential scanning calorimetry. Representative examples of such reaction pathways during crystallization of 3 LDS and LS variants are illustrated in Figure 1.

**IPS e.max CAD.** LDS glass–ceramic CAD blocks consist of lithium metasilicate ( $Li_2SiO_3$ ) crystals ( $\sim 40$  vol%) embedded in a glass matrix, with  $P_2O_5$  nucleant and  $CeO_2$  colorant. During firing, the glass matrix partially crystallizes to cristobalite ( $SiO_2$ ) at  $\sim 660$  °C, which converts at  $\sim 735$  °C to  $Li_2Si_2O_5$  crystallites ( $Li_2SiO_3 + SiO_2 \rightarrow Li_2Si_2O_5$ ), with final precipitation of Ce oxide at  $\sim 775$  °C. The microstructure of the resulting glass–ceramic consists of  $\sim 70$  vol% crystalline phase in the form of elongated  $Li_2Si_2O_5$  rods (major phase), equiaxed  $Li_3PO_4$  blocks (minor phase), and some small cubic  $CeO_2$  crystals (Ortiz et al. 2019).

**Obsidian.** These LS CAD blocks consist of dendritic  $Li_2SiO_3$  nanocrystals in a glass matrix. Upon heating, the glassy matrix does not crystallize into any form of  $SiO_2$ ; elemental oxides do not precipitate; and the nanocrystals do not form typical LDS microstructures. Instead, the nanocrystals spheroidize through a solution–reprecipitation process in the softened glass. The resulting microstructure consists of  $\sim 43$  vol% submicrometer round  $Li_2SiO_3$  ( $< 500$  nm, major phase) and  $Li_3PO_4$  crystals ( $< 100$  nm, minor phase) (Ortiz et al. 2020).

**Suprinity PC.** Biphase LDS/LS CAD blocks are initially sintered lightly to form  $Li_2SiO_3$  nanocrystals in partially depolymerized zirconosilicate glass. Upon heating to  $\sim 810$  to  $820$  °C, the glass reacts with a portion of the  $Li_2SiO_3$  to form  $Li_2Si_2O_5$ . Shortly after,  $Li_3PO_4$  precipitates from the glass. This results in a fine-grained glass–ceramic with a  $\sim 57$  vol% nanocrystalline phase embedded in a zirconosilicate glass matrix (Ortiz et al. 2021).

### Forming

One of the advantages of the glass–ceramic crystallization process is the potential for achieving near net shape forming, critical to ensure that the crystallization heat treatment does not lead to restoration distortion. Ordinarily, glass-to-crystal transformation can be accompanied by significant shrinkage (Zanotto and Mauro 2017). However, firing of IPS e.max CAD restorations results in virtually no deformation with very small shrinkage ( $\sim 0.2\%$  vs.  $\sim 20\%$  sintering shrinkage of zirconia; Lim et al. 2022). The key to mitigate against shrinkage is to maintain high glass viscosity throughout the crystallization process (Fu et al. 2016), typically around 2 orders of magnitude greater than that at the glass-softening temperature. One way to achieve this is to precrystallize the glass.

This is an area of materials science that is receiving more attention as dental glass–ceramics continue to evolve.

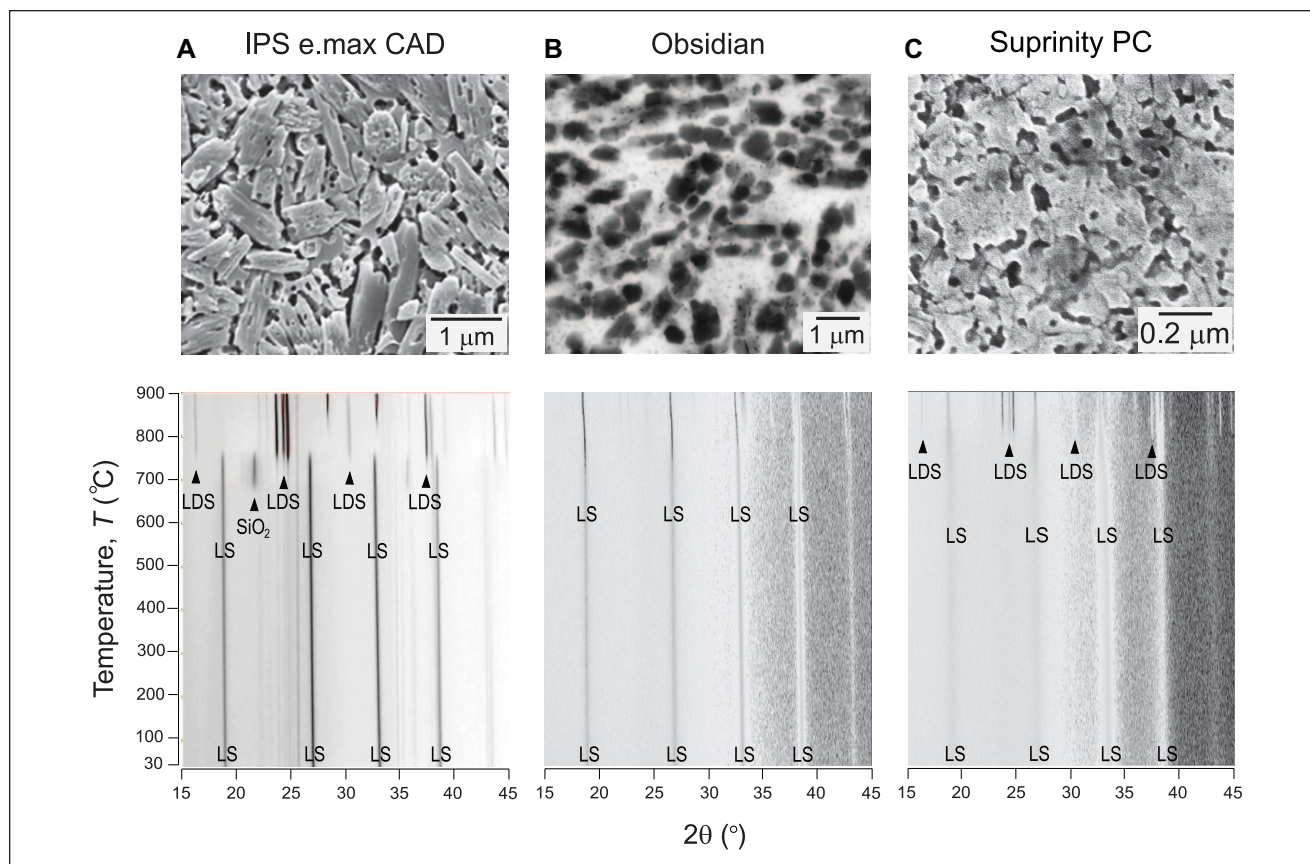
## Clinical Issues

### Failure Rates

A survey on materials of choice for a single-unit crown was conducted by the National Dental Practice-Based Research Network in the United States (Makhija et al. 2016). An overall 1,777 eligible dentists responded, and LDS glass–ceramics consistently emerged among the top 3 materials of choice. For anterior crowns, LDS (54%) led layered zirconia (17%) and leucite-reinforced glass–ceramic (13%), whereas for posterior crowns, LDS (21%) closely trailed monolithic zirconia (32%) and porcelain fused to metal (31%). Unsurprisingly, there has been a large number of clinical reports on the usage of lithia glass–ceramics, specifically IPS e.max Press and CAD. However, data concerning restoration survivability are not always consistent across studies (Rekow et al. 2011). Many factors can affect survival rates, such as tooth condition and position, restoration type, patient factors, dentist skill, sample size, and follow-up duration.

As indicated, most systematic survival studies of lithia dental prostheses have been conducted on IPS e.max. One particular study program (Kern et al. 2012; Garling et al. 2019) examined the survival rates of 36 monolithic IPS e.max Press 3-unit fixed dental prostheses (FDPs): 24 molars, 6 premolars, and 6 anterior teeth. No fractures occurred in the first 6 y, but the survival rate was 87.9% at 10 y and declined rapidly to 48.6% at 15 y. Such prolonged decline presents a strong case for long-term clinical studies. A more expansive study program





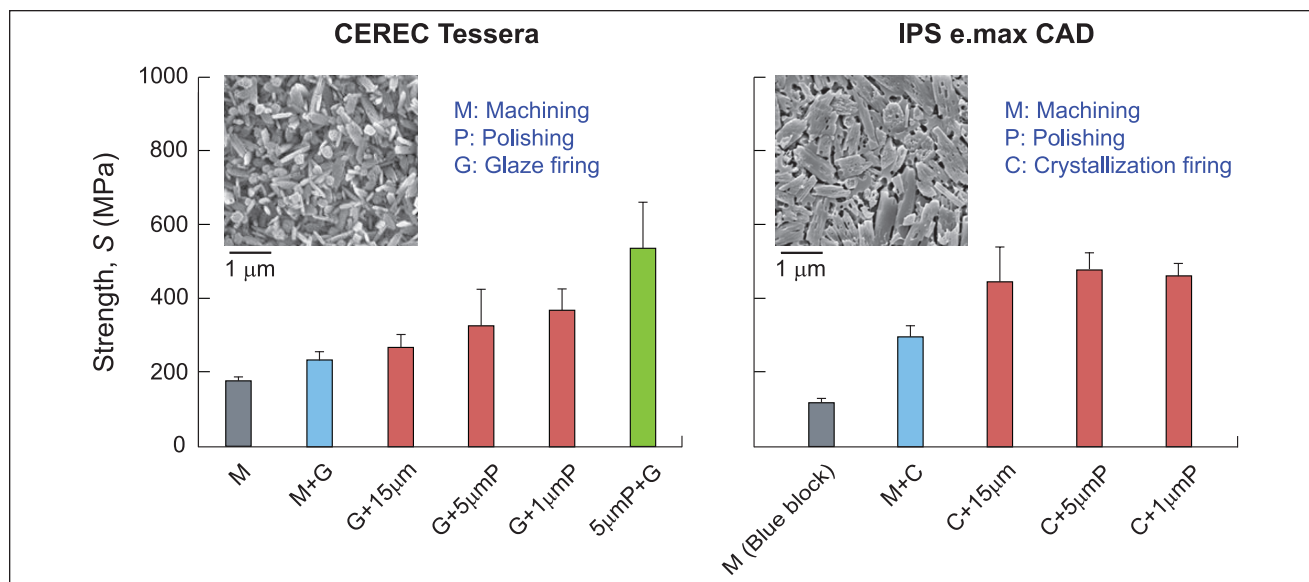
**Figure 1.** Microstructure and compositional evolution of 3 representative lithia glass–ceramic variants: **(A)** IPS e.max CAD (Ortiz et al. 2019), **(B)** Obsidian (Ortiz et al. 2020), and **(C)** Suprinity PC (Ortiz et al. 2021). Scanning electron microscopy images show crystal morphology and microstructure (upper row). Specimen surfaces finished with 1- $\mu\text{m}$  diamond suspension polish and chemically etched with 5% hydrofluoric acid. X-ray thermodiffraction spectra collected in situ as a function of temperature ( $T$ ), for  $2\theta = 15^\circ$  to  $45^\circ$ , show phase transformations (lower row). LDS, lithium disilicate; LS, lithium silicate;  $\text{SiO}_2$ , cristobalite.

on IPS e.max Press partial coverage restorations ( $n = 566$ ) and complete coverage restorations ( $n = 1960$ ; Malament et al. 2021a, 2021b) reported rates for posterior inlays and onlays of 93.6% and 98.3% at 9.8 y; for partial coverage restorations with dental arch in the mandible, it was 88% at 9.2 y; and for complete coverage restorations, the overall survivor rate was 96.5% at 10 y, but for mandibular second molars, it was only 87.5% at 7.3 y. In general, the survival rate for implant-retained monolithic LDS complete coverage crowns was slightly lower, 91% at 5 y (Sailer et al. 2022). Evidently, higher fracture rates of LDS restorations for molar teeth and 3-unit FDPs suggest that damage resistance of lithia glass–ceramics needs further improvement.

There are not yet systematic long-term clinical studies on other variants of lithia glass–ceramics, but a short-term study on Celtra Duo chairside restorations revealed 26% terminal fractures at just 1 y (Christensen 2018). Clearly, plenty of room remains for dental researchers and clinicians to collect data and to explore the fundamentals of glass–ceramic composition and microstructure while developing new fabrication technologies.

### Preparation Factors

Despite its reputation as the most widely used dental glass–ceramic in current use, IPS e.max CAD has acknowledged preparatory shortcomings in the ever-evolving world of digital dentistry. Precrystallized blocks are susceptible to microcrack flaws from grinding damage. In extreme cases, restorations  $<0.7\text{-mm}$  thickness become prone to catastrophic fracture during CAD/CAM grinding. Margins of ground restorations are susceptible to chipping (Tsitrou et al. 2007), which can result in infiltration and discoloration of the tooth–restoration interface (Fasbinder et al. 2010; Willard and Gabriel Chu 2018) or, in extreme cases, complete restoration fracture (Tsitrou et al. 2007; Brandeburski et al. 2020). To avoid these issues, many technicians stop short during CAD/CAM grinding and then handpiece grind the restoration to the desirable thickness. However, hand grinding inevitably compromises the accuracy of fit. Others resort to the lost-wax heat press method for fabricating thinner restorations, but this route is labor intensive and time consuming.



**Figure 2.** Biaxial flexure strength of CEREC Tessera and IPS e.max CAD with various surface finishes ( $n = 10$  per column). Tests were performed on disc specimens ( $\varnothing 12 \times 1$  mm) loaded in a piston-on-3-ball fixture (piston radius, 0.7 mm; 3-ball support circle radius, 4 mm) with a universal testing machine (crosshead speed 1 mm/min; Instron 68TM-5). From left to right: M, CAD/CAM machining; M+G, CAD/CAM machining + glaze firing; G+15 µm, glaze firing + 15-µm grinding; G+5 µmP, glaze firing + 5-µm finish polishing; G+1 µmP, glaze firing + 1-µm finish polishing; 5 µmP+G, 5-µm finish polishing + glaze firing; M, CAD/CAM machining (blue block); M+C, CAD/CAM machining + crystallization firing; C+15 µm, crystallization firing + 15-µm grinding; C+5 µmP, crystallization firing + 5 µm finish polishing; C+1 µmP, crystallization firing + 1-µm finish polishing. Data are presented as mean  $\pm$  SD.

There would appear to be a strong case for developing less invasive grinding protocols that avoid damage to the restoration in the first place.

## Mechanical Properties

### Strength

The resistance to catastrophic failure in any brittle material is quantified by strength  $S$  (MPa): the tensile stress at which catastrophic fracture initiates from flaws, either inbuilt into the microstructure or from subsequent surface preparation (Lawn 1993). Strength values are typically cited for highly polished specimens, representing failure from intrinsic microstructural flaws. Such strengths tend to be a best-case scenario. Dental restorations typically experience different levels of surface finish, which can degrade strength. For instance, the intaglio surface of a crown or FDP is never polished, leaving deleterious subsurface grinding damage.

To illustrate, Figure 2 compares biaxial flexure  $S$  values of lithia silicate CEREC Tessera versus IPS e.max CAD for various combinations of machining and lap polishing (grit sizes indicated), glazing, and crystallization. Biaxial tests on disc specimens were used instead of conventional 3-point flexure tests on bars to avoid edge failures. The discs ( $\varnothing 12 \times 1$  mm,  $n = 10$ ) were mounted in a piston-on-3-ball biaxial jig loaded on a universal testing machine (Instron 68TM-5) with a crosshead speed of 1 mm/min.  $S$  for CAD/CAM machined specimens increases with polishing as grit size is refined from 15 to

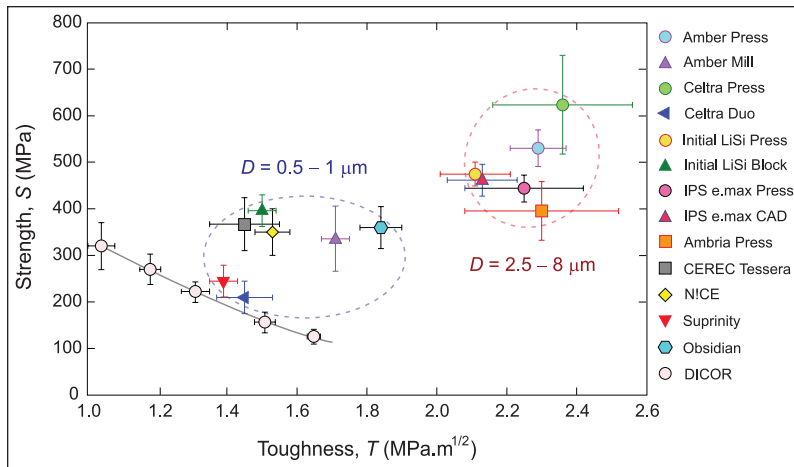
1 µm. For CEREC Tessera, glazing also increases  $S$ , more notably if conducted after polishing, ostensibly to heal remnant surface fissures. IPS e.max CAD benefits from crystallization after machining but appears to be somewhat less sensitive to grit size in subsequent grinding and polishing. It is noteworthy that CAD/CAM machining drops nominal strength by over a factor of 2 in these and other glass–ceramics. Thus, any advance in grinding technology that minimizes surface damage would appear to be highly desirable.

It is apparent that strength properties can be complex, so resorting to evaluations from routine standardized tests of as-polished specimens may not always be a reliable indicator of ultimate performance.

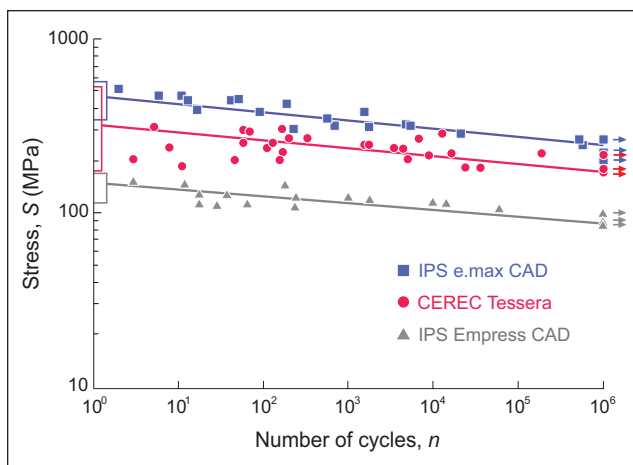
### Toughness

Strength is not the only important mechanical measure of structural integrity. The resistance to the propagation of a crack once it has formed is quantified by toughness  $T$  (MPa·m<sup>1/2</sup>; Lawn 1993). In prostheses such as dental crowns, longitudinal cracks tend to extend slowly and stably with increasing bite force and can remain contained along the side walls without fully fracturing the structure (Zhang et al. 2016). Consequently, it is desirable to maximize  $T$  to inhibit cracks from traversing entire prosthetic structures.

Strength and toughness are interrelated but not necessarily in a direct proportional way. This is illustrated in Figure 3 for different glass–ceramics with finely polished surfaces (1-µm grit). For the original DICOR glass–ceramic, there is an inverse



**Figure 3.** Biaxial flexural strength ( $n = 10$ ) versus fracture toughness (mean  $\pm$  SD) for the suite of commercial lithia glass-ceramic materials in Table, with comparative values for DICOR (Lawn 2004). For lithia glass-ceramics, fracture toughness values were obtained from Lubauer et al. (2022), while biaxial flexure strength was measured in our laboratory. Again, tests were performed on disc specimens ( $\varnothing 12 \times 1$  mm) loaded in a piston-on-3-ball jig with a universal testing machine (Instron 68TM-5) with a crosshead speed of 1 mm/min. To facilitate direct comparisons, the tensile surface of all test specimens was finished with 1- $\mu$ m diamond suspension polish.  $D$ , mean crystal size.



**Figure 4.** Biaxial flexural stress as a function of number of cycles to failure for IPS e.max CAD (squares), CEREC Tessera (circles), and IPS Empress CAD (triangles) glass-ceramic materials at 2 Hz in water. Tests were performed on disc specimens ( $\varnothing 12 \times 1$  mm,  $n = 40$ ), with the tensile surface prefinished with 1- $\mu$ m diamond suspension polish. Solid lines are linear best fits to experimental fatigue data in accordance with a slow crack growth model. Open boxes on the vertical axis indicate intrinsic single-cycle biaxial flexural strength values. Arrows to the right represent runouts.

correlation, as the grain size ( $D$ ) increases with extended heat treatments (Lawn 2004). Interestingly, this inverse microstructure-dependent relationship is not observed among the disparate lithia glass-ceramics with their different starting compositions. In fact, the group of coarser microstructures ( $D > 2 \mu\text{m}$ ) appears to yield significantly higher  $T$  values than their fine-grain counterparts but with commensurately higher  $S$  values. This is

counterintuitive, as coarser microstructures are usually associated with larger flaw sizes. It implies that factors beyond microstructural scale can dominate, such as base glass composition and glass-crystal interface properties. Thus, those newer fine-grained variants that have been advocated for CAD/CAM grinding, polishing, and seating without any postshaping heat treatment (e.g., Celtra Duo, Initial LiSi Block, N!CE) exhibit relatively low  $S$  and  $T$ , suggesting that they may actually be more susceptible to processing and handling damage.

## Fatigue

We have indicated that material properties from static laboratory tests may not provide a significant indicator of restoration longevity. Indeed, properties of glass-ceramics can undergo progressive degradation from crack growth under sustained loading (i.e., fatigue). Cyclic tests on flexure specimens in aqueous solutions offer a simple but powerful way to demonstrate the extent of such degradation.

Figure 4 plots stress  $S$  for 3 lithia glass-ceramics as a function of number of cycles  $n$  to spontaneous failure in biaxial flexure. Data are for disc specimens ( $\varnothing 12 \times 1$  mm,  $n = 40$ ) with 1- $\mu$ m diamond-polished tensile surfaces, tested on a mouth-motion fatigue machine (ElectroForce 3330; TA Instruments).  $S$  values of these glass-ceramics (and indeed all oxide ceramics) typically degrade by up to a factor of 2 to 3 over a million loading cycles (Zhang et al. 2013). In this case, the steady degradation of  $S$  is attributable to cumulative slow crack growth from intrusion of water molecules into surface flaws (Wiederhorn 1967).

But simple flexure tests do not tell the whole story. Additional mechanisms of a mechanical nature can greatly exacerbate fatigue well beyond that in Figure 4, especially in contact (occlusal) loading (Zhang et al. 2013).

## Future of Lithia Glass-Ceramics

### Material Development

In the high-strength dental ceramic market, lithia-based glass-ceramics have a competitor, namely zirconia. Zirconia ceramics have higher strength and toughness, especially for compositions with lower yttria contents (i.e., 3 to 4 mol%; Zhang and Lawn 2018), making them the most durable crown and FDP materials (Christensen 2018). However, lithia glass-ceramics have superior aesthetics, owing to their greater translucency and range of color shade selections. They also have the capability to form strong adhesive resin bonding through traditional acid etching and silanization processes (Blatz et al. 2018). Accordingly, efforts are underway to strengthen lithia glass-ceramics through microstructural tailoring (Hallmann



et al. 2018) and 3-dimensional (3D) nanoarchitecture designing (Fu et al. 2017).

The sheer number of lithia products listed in the Table attests to the potential diversity of glass–ceramic variability. Among the several production variables are glass composition, processing nucleants, crystallization heat treatment, and shaping protocols. Figure 3 demonstrates that lithia-based glasses yield superior mechanical properties relative to those of micaceous-based DICOR glasses. This can be partly attributed to stronger intrinsic bonding with lithium ions within the atomic superstructure and at the crystal–glass interfaces. Such a range of fabrication variables leaves open the prospect of further advancement in material development, with ever-improving mechanical and aesthetic properties.

Are lithia-based ceramics the only route to this end? Again, this is a rich field for the materials scientist.

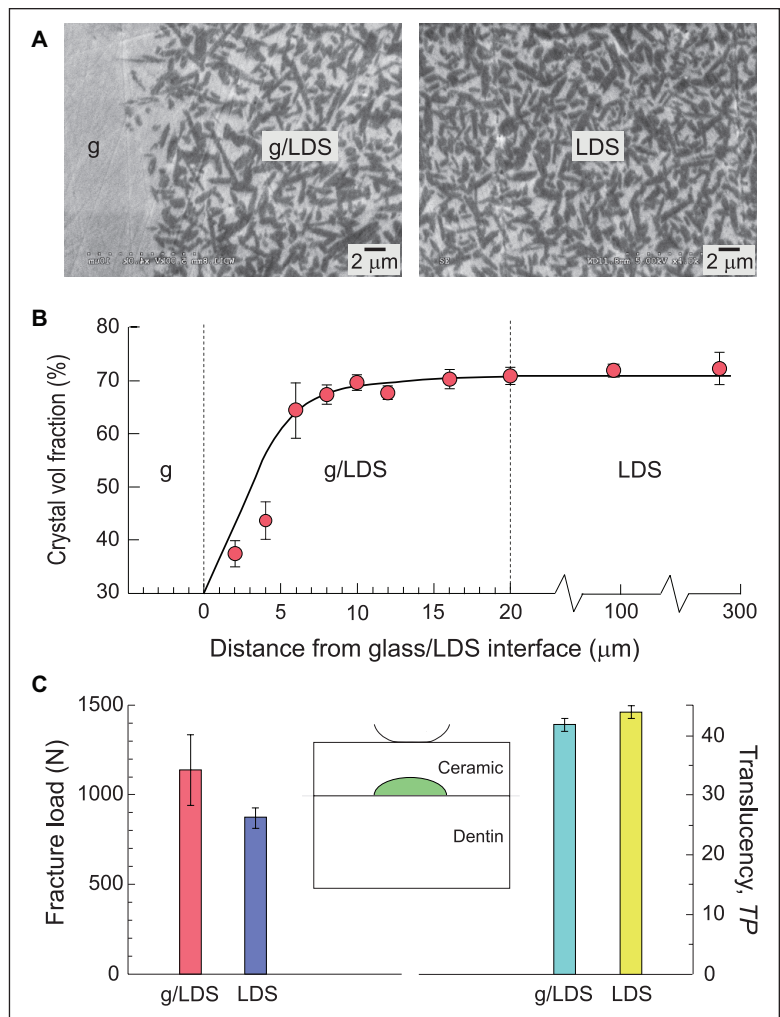
### Graded Glass–Ceramics

An advantage of lithia silicates is that their elastic moduli are better matched to the underlying tooth support relative to stiffer zirconia or alumina competitors, enabling greater load-bearing capacity (Ma et al. 2013). This capacity can be enhanced by judiciously grading the cementation intaglio surface of LDS by infiltration with a lower modulus glass to “cushion” an applied load. To demonstrate, precrystallized LDS discs ( $\varnothing 12 \times 1$  mm,  $n = 8$ ) were uniformly coated with a feldspathic glass (IPS e.max CAD Crystall Glaze Spray) and crystallized at 840 °C (Bhavishetty 2018). The glass-infiltrated surface of the disc was resin cemented (Multilink Automix; Ivoclar Vivadent) to a dentin-like composite substrate (NEMAG10; International Paper). Load was applied on the top surface of the LDS disc with a stiff tungsten carbide indenter ( $r = 3.18$  mm; Yan et al. 2018). Figure 5 shows cross-section images for an IPS e.max CAD specimen ( $E = 103$  GPa) surface infiltrated with a lower-modulus glass ( $E = 60$  GPa); crystalline content over the graded interface with a thin residual glass surface layer; and the load-bearing capacity of a disc supported on a substrate ( $E = 18$  GPa). The load to fracture is  $\sim 30\%$  higher for infiltrated specimens, with no adverse effect on translucency.

Such data are highly suggestive of additional improvements in durability by alternative surface modification treatments, such as introduction of surface compressive stresses (Li et al. 2020).

### “Ductile” Machining

CAD/CAM shaping and diamond bur finishing technologies have not kept pace with material development. Current



**Figure 5.** Microstructure and properties of surface glass-infiltrated IPS e.max CAD. **(A)** Scanning electron microscopy cross-section views of external glass (g), graded zone (g/LDS), and interior LDS. **(B)** Volume fraction (mean  $\pm$  SD) of LDS crystals as a function of distance from the glass interface ( $n = 6$ ). **(C)** Fracture load in bilayer loaded with a tungsten carbide sphere for 1-mm discs on dentin-like substrate ( $n = 8$ ) with a crosshead speed of 1 mm/min and translucency parameter ( $TP$ ;  $n = 6$ ) for infiltrated (g/LDS) and uninfiltrated (LDS) discs. LDS,  $\text{Li}_2\text{Si}_2\text{O}_5$ .

protocols used for fluted carbide bur milling of green zirconia and for diamond grit bur grinding of partially crystallized glass–ceramics and fully crystallized/sintered ceramics introduce subsurface microcrack-like defects, compromising strength (Curran et al. 2017; Romanyk et al. 2019). Subsequent polishing steps can go some way to remove excess machining damage; however, polishing is time consuming and is not guaranteed to eliminate deeper microcracks (Kou et al. 2006; Alao et al. 2017). Moreover, the intaglio surface of a crown or FDP is never polished since it is difficult to access the inner region (Helvey 2011). In addition, laboratory-fabricated restorations, including 3D printed or heat-pressed prostheses, almost always need some adjustments by grinding, further introducing strength-degrading defects (Canneto et al. 2016; Curran et al. 2017; Vila-Nova et al. 2020).

Machining theory predicts that there exists a region between grinding and polishing where material can be effectively removed at an acceptably fast rate without incurring strength-degrading damage—a regime known as “ductile grinding” (Bifano et al. 1991; Huang et al. 2021). In this region of grinding, microcracks may still form within a ductile chip but not penetrate below the cut surface (Lawn et al. 2021). The key is to optimize depth of cut and grinding speed. The potential benefits of ductile grinding include better restoration contour accuracy, a smooth surface finish that can make the subsequent polishing unnecessary, a material removal rate >3 orders of magnitude faster than polishing, retention of ceramic strength, and preservation of diamond burs. While ductile grinding is receiving major attention in the manufacturing sector, it has not yet been successfully applied in dentistry (Lawn et al. 2022).

### Additive Manufacturing

Additive manufacturing (AM) or 3D printing offers a remedy for limitations of current CAD/CAM machining technology, notably for introduction of strength-limiting subsurface damage and material wastage. An attractive aspect of AM technology is flexibility in design algorithms, where meshes of geometrical parameters, material compositions, degrees of translucency, and even colors and shades can be controlled for optimal properties. Although 3D printing has now been integrated into the CAM hardware as an alternative to subtractive machining (Rekow 2020), only a few commercial material systems indicated for permanent restorations are suitable.

3D-printed and laser-sintered base metal frameworks are clinically available for fixed metal–ceramic restorations and removable partial dentures. Some polymer-based systems have emerging applications as interim fixed or removable prostheses, occlusal splints, wax patterns, surgical guides, and study models (Anadioti et al. 2022). While no such AM systems are widely available for ceramic-based restorations, a number of related printing techniques have demonstrated potential. They include direct inkjet printing (DIP), stereolithography, selective laser melting/sintering, and direct energy deposition (Galante et al. 2019). All have their own limitations—porosity and flaw populations are high, thus diminishing strength and translucency (Fu et al. 2020). In addition, DIP and selective laser melting/sintering have poor shape accuracy, whereas DIP and stereolithography involve prolonged drying, debinding, and crystallization/sintering processes.

AM of dental prostheses remains a technology in progress.

### Conclusions

In this article, we draw the following conclusions. First, lithia-based glass–ceramics represent a widely used class of dental restorative ceramic materials. They possess excellent aesthetics and respectable strengths and are suitable for time-efficient digital fabrication. Second, fine-grained variants indicated for grind and seat without any postshaping heat treatment exhibit

relatively poor mechanical properties. Third, next-generation glass–ceramics with enhanced aesthetic and mechanical properties will continue to evolve as base glass compositions and heat treatments are refined. Fourth, innovative machining and finishing protocols will be critical factors in the optimal application of lithia glass–ceramics in clinical settings. Finally, novel fabrication methodologies such as surface gradation and 3D printing offer the prospect of more efficient and longer life-time restoration ceramics.

### Author Contributions

Y. Zhang, contributed to conception and design, data acquisition, analysis, and interpretation, drafted and critically revised the manuscript; S. Vardhaman, C.S. Rodrigues, contributed to design, data acquisition and analysis, critically revised the manuscript; B.R. Lawn, contributed to conception and design, data analysis and interpretation, critically revised the manuscript. All authors gave final approval and agree to be accountable for all aspects of the work.

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