São Carlos Center of Research, Technology and Education in Vitreous Materials

The first four years

CeRTEV is an 11-year, approximately $22 million effort with funding of about $2 million per year through 2018, after which the São Paulo State Research Foundation will evaluate the program before authorizing funding for the following six years. In a Ceramic Tech Today post from 2013 (www.ceramics.org/ceramic-tech-today/52681), the Center's director, Prof. Edgar D. Zanotto, said "We believe this will give us some momentum… We expect the project will catalyze some energy, some new efforts, and perhaps motivate some young people to enter the field. Let's talk in three years and see how things are going. At least for Brazil, it will likely have a large impact. As to the international glass science, let's see. I hope so!"

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Four years have passed since the Center of Research, Technology and Education in Vitreous Materials (CeRTEV, www.certev.ufscar.br) was founded with a generous grant of the São Paulo State Research Foundation (FAPESP), as part of the state's comprehensive Centro de Pesquisa, Inovação e Divulgação (CEPID) program, from which seventeen of such centers covering diverse areas of knowledge were created in 2013. Ours is one of the smallest CEPIDs, but it has built one of the largest academic glass research teams in the world!

CeRTEV comprises 14 professors (9 are principal investigators): 6 at the Federal University of São Carlos (UFSCar) and 7 at the University of São Paulo (USP), both located in São Carlos, Brazil; and 1 at São Paulo State University (UNESP), located in the city of Araraquara, 35 km from São Carlos, Brazil. These professors are experts in engineering, chemistry, and physics of vitreous materials, including glass structure, crystallization kinetics, wide-ranging structural and functional characterization, as well as manufacturing techniques. They advise about 60 students and post-docs engaged in glass research and are embedded in a large Brazilian and international network of collaborations. UFSCar serves as the host institution, although facilities have been built in partner labs of all participating universities. CeRTEV's scientific, technological, and educational progress is being monitored by an International Advisory Board (IAB) consisting of 22 international leaders in glass science and industry. Valuable recommendations from the IAB have been added regularly to complement the center's agenda, and many board members have also become scientific collaborators in the meantime. Recently, a team of advisors belonging to different Brazilian industrial glass segments was created in CeRTEV to tailor our activities to national demands.

1. Mission of the Center

CeRTEV's mission is to conduct state-of-the-art research, technology development, education, and outreach on glass and glass-ceramic materials. We aim to include and keep Brazil among the top 10 glass research countries in the world. We also intend to include São Carlos in the world map of glass science cities, which currently includes Sheffield, Alfred, Corning, Jena, St. Petersburg, Kyoto, Tokyo, Nagaoka, Paris, Rennes, Montpellier, Kolkata, Wuhan, and a few others. As part of the joint CeRTEV research agenda, the 14 faculty work together to develop new glasses, glass-ceramics, composites, and hybrid materials, presenting relevant functionalities—such as high mechanical strength, electrical conductivity, biological, optical or catalytic activity, and/or combinations of these properties—guided to different applications.

CeRTEV's agenda is divided into five core areas dedicated to the principal fields of glass and glass-ceramic applications:

1. Structural materials for architecture, construction, armor, and dental restoration;

2. Bioactive glasses and glass-ceramics for bone and cartilage healing and growth;

3. Ion-conducting materials for applications in modern battery and energy technologies;

4. Photonic glasses and glass-ceramics; and

5. Catalytically active systems.

All these application areas benefit from research encompassing development of fundamental concepts regarding the structural description of glasses and structural, dynamic (diffusion, relaxation, and viscous flow), and mechanistic aspects of the processes involved in crystallization of glasses leading to glass-ceramics.

On the technology side, CeRTEV activities are channeled towards generation of new technologies and patents, all the way to new products and manufacturing processes—a "science to business approach." Thus far, new or improved patentable glass or glass-ceramic materials have been developed for light armors (for use in airplanes and cars and by individuals), solid electrolytes for electrochemical devices, tougher monolithic glass-ceramics for dental restoration, macroporous and hierarchically ordered scaffolds, fibers, small monolithic parts, and powders with increased osteoinductive activities combined with the ability for targeted drug delivery for bone and tissue repair. Efforts in extending the development of technologies for applications related to other CeRTEV research areas are underway.

CeRTEV's education and outreach strategies focus on development of long-term sustainability of glass science and technology in Brazil. At present, lack of training courses dedicated to professionals in the glass industry seriously impinges its development. To remedy this situation, we have developed a comprehensive curriculum for a new technical course in cooperation with Brazilian professional organizations. In parallel, we have mounted an aggressive effort of public promotion of the importance of glass and glass-ceramics. Our educational activities include development of educational kits, mutual visitation projects with high schools, participation in science fairs, design of visually attractive display banners and science comics, as well as theater presentations that we call "science on stage."

2. Research activities and highlights

A top priority for CeRTEV's success has been development of a coherent research program aligning the activities of its individual members with common CeRTEV objectives. Towards this purpose, bi-monthly planning meetings have taken place during the past two years, and joint activities are now in full force. About 34% of our current publication output originates from collaborative research involving two or more CeRTEV faculty members.

Regarding aspects of fundamental glass science, our efforts concentrate on understanding the structural and mechanistic aspects of nucleation and crystallization processes for development and improvement of glass-ceramics, and on general study of structure/property relations in the five aforementioned application areas. These efforts include technique development, such as new potentials for molecular dynamics (MD) simulations, new differential scanning calorimetry (DSC) approaches, advanced solid state magnetic resonance (NMR, EPR) methodology, and Raman spectroscopies. Below we describe the main lines of our joint research, highlight some key results, and indicate further directions to be pursued in the near future.

2.1. Fundamental glass science

New insights into glass structure and crystal nucleation, growth, and overall crystallization of oxide glasses are the stronghold of CeRTEV's international reputation. In solving an 80-year old question, we were able to demonstrate that albite and B_2O_3 glasses—the most stable oxide glasses ever reported—do not crystallize because of their extremely low thermodynamic driving force for (homogeneous) nucleation in the glass transition region [1]. In this region, we have characterized dynamic heterogeneities, which may have a fundamental role on the size of critical crystalline nuclei and may explain the often reported breakdown of classical nucleation theory near the glass transition temperature [2]. Finally, analyzing a wide range of thermodynamic and structural data, we were able to show that the homogeneous nucleation mechanism can be favored over a heterogeneous one only in those glasses in which the network short- and medium-range order around modifier species in the glass closely resembles that in the isochemical material crystallizing from it [3].

Structure–property relations have been examined over the full range of length scales (micrometers to angstroms) in all of CeRTEV's topical areas. We found that strength and toughness of lithium disilicate (LS2) glass-ceramics can be controlled by the crystallized volume fraction (for a fixed grain size). Our results reveal the most effective mechanisms for toughening and outline microstructural conditions necessary for optimum mechanical stability [4]. In the area of ionically conducting glasses, NMR results show that the well-documented network former mixing (NFM) effect is based on phenomena at the scale of medium-range order—a positive NFM effect (enhanced ionic conductivity) is associated with preferred heteroatomic connectivities, facilitating more effective charge dispersal. In contrast, negative NFM effects only occur in systems with preferred homo-atomic network linkages (incipient nano-segregation) [5]. Finally, emission characteristics of photonic glasses can be understood on the basis of direct atomic environments of active rare-earth dopant ions, as revealed by correlated NMR, EPR, and Raman spectroscopy [6]. For glass structure simulations, new potentials were developed for barium disilicate melts, producing excellent agreement with experimental neutron diffraction structure factors and the vibrational density of states [7]. Finally, there is new experimental support for the weak electrolyte theory of ionic transport in glasses, which assumes that effective charge carriers are defects comparable to vacancy/interstitial site pairs in ionic crystals. These pairs result from partial dissociation of ionic glass components, such as network modifiers or halide salts. New electrochemical cells have been designed to measure the thermodynamic activity of these ionic components in xAgI (1-x)$AgPO_3$ glasses, which show a five-fold increase of ionic conductivities over the composition range ($0 \leq x \leq 0.5$). Our experimental results reveal a linear correlation between thermodynamic activities and ionic conductivities at constant total Ag^+ content, suggesting that the effective charge carriers are indeed generated by a simple dissociation equilibrium of AgI [8].

2.2. Strong glasses and glass-ceramics for armor and dental applications

Aside from the aforementioned fundamental work on LS2 armor ceramics [4], further highlights in this area include development of new formulations for multiphase glass-ceramics and characterization of their extremely promising mechanical stabilities. We developed a brand new and difficult to make transparent magnesium aluminosilicate glass-ceramic intended for armor applications and evaluated its elastic properties at low and high temperatures. Results of the first ballistic tests are very promising [9]. We also studied homogeneous crystallization of a new series of lithium calcium silicate glasses in the absence of nucleation agents [10]. A composition of 44 mol% $CaSiO_3$ heat-treated at 498 °C for 24 h for nucleation and at 700 °C for 2 h for crystal growth results in a (nucleant-free) glass-ceramic with outstanding mechanical properties for load-bearing applications [10].

2.3. Bioactive glasses and glass-ceramics

Research at CeRTEV on bioactive glasses focuses on the continuing improvement of osteoconductive and osteoinductive materials for stimulating bone healing and growth by developing and testing new bioactive formulations and composites, such widened applications for Biosilicate® in bone repair and dental restoration [11,12]. Recent histopathology, cytotoxicity, and genotoxicity analyses have confirmed that Biosilicate® affects osteoblast expression of genes associated with the process of mineralization, highlighting their osteostimulatory properties [13]. We are further continuing to explore compositional effects on various aspects of bioactivity performance, particularly regarding substitution of calcium by magnesium or strontium, and examination of boron-containing bioactive glasses. CeRTEV's most recent outstanding achievement in bioactive glass was development of a new glass formulation ("F18") that allows large-scale continuous fabrication of glass fibers via processing techniques such as downdrawing [14]. Besides bioactivity and high reactivity, F18 also presents a remarkable and highly desired bactericidal effect. F18 development opens new venues in tissue engineering and in creation of novel medical devices for clinical applications, including membranes for skin wound regeneration, nerve guide conduits, and scaffolds with high porosity. Also, in vivo tests show osteoinductive and osteopromotive activity, making this glass a potential bone-grafting material for many clinical applications [14].

2.4. Glasses and glass-ceramics for high-energy storage devices

Ion-conducting NASICON glass-ceramics based on lithium titanium phosphate and lithium germanium phosphate have already attracted commercial interest as membrane separators in lithium/air batteries. Using isovalent and aliovalent substitution strategies, we have contributed to new homogeneously crystallizing formulations with competitive ionic conductivities [15, 16]. Modern solid-state NMR techniques have provided important insight into the influence of the crystalline fraction on ionic mobility and electrical conductivity [15,17]. Currently, we are developing glass-ceramic routes for preparation of sodium-containing superionic conducting materials. This work is motivated by a much higher abundance of sodium as compared to lithium in the earth's crust. Successful preparation of single-phase crystalline compounds with additional incorporation of Na^+ ions was accomplished through aliovalent substitution in either cationic or anionic sub-lattices [17], leading to significantly enhanced ionic conductivities. Along similar lines, we will explore oxy-chalcogenide glass compositions that form superionic crystals upon ceramization.

2.5. Photonic glasses and glass-ceramics

CeRTEV's activities in photonic glasses and ceramics focus on development and characterization of new systems doped with luminescent species (transition or rare-earth metal ions, metal nanoclusters) for applications in lasers, sensors, and other photonic devices. The structural environments of rare-earth ionic species in fluoride phosphate matrices have been studied by newly developed NMR and EPR approaches, leading to an understanding of their photophysical characteristics in terms of ligand distribution around rare-earth ions [6,18]. New rare-earth-doped glass formulations based on fluoride phosphate and -tellurite matrices have been developed for laser applications and white-light generation. Radiative properties of these materials are comparable to the best results currently available in the literature [18]. These glasses are also highly suitable candidates for converting ultraviolet and infrared light of the solar spectrum into visible light, improving energy harvesting by c-Si solar cells [19]. Absorption, luminescence, and electron spin resonance spectroscopies have been used to obtain new mechanistic insights on the photosensitization process of rare-earth emission by metallic nanoparticles [20], on growth kinetics of these nanoparticles by in-situ monitoring [21], on intriguing valence changes upon ceramization of heavy metal oxide glasses [22], and on the photo-ionization process in photothermal refractive (PTR) glasses [23].

Another area of active research within CeRTEV is development of new photonic inorganic–organic hybrid materials and nanocomposites. Besides offering the possibility of designing a more favorable chemical environment to improve the photophysical properties of guest molecules, encapsulation in solids also protects such emitter molecules, preventing their leakage (especially critical for biological applications) and ultimately leading to more robust and versatile materials [24].

2.6. Catalytic systems

An entirely new application field of glass-ceramics is being developed in the fifth topical CeRTEV research area devoted to catalytically active systems for conversion of biomass to fuel and fine chemicals. Here we aim to design hierarchically structured glass-ceramics combining mesoporosity (for catalytic conversions) with macroporosity (for facilitating mass transport of highly polymerized substrates). Techniques under development include: (a) ceramic foaming based on the use of porogenic agents; (b) selective leaching of phase-separated glasses; and (c) sol-gel techniques using molecular precursors. In the latter area we are harvesting synergetic benefits with ongoing work aimed at porous optical and bioactive materials.

2.7. Highlights

As a result of all this research activity, CeRTEV's 9 PIs have published about 145 original and review articles related to vitreous materials in the past 4.5 years, which accounts for approximately 15%–20% of all "glass" articles produced in Brazil in this same period. We have also organized or co-organized several international workshops and symposia on glass, sol-gel, glass crystallization, photonic materials, and honor sections, including the Don Uhlmann Festschrift in Madison in 2016 and The Larry Hench Memorial symposium in Sheffield in 2016. Finally, CeRTEV's coordinator is currently serving as chair of the Glass and Optical Materials Division (GOMD) of the American Ceramic Society.

3. Innovation and knowledge transfer

CeRTEV's "science to business" agenda encompasses all application fields of our research program:

1. Strong glass-ceramics for armors and dental implants;
2. Bioactive materials for bone and tissue restoration;
3. Energy storage and conversion systems;
4. Photonic devices; and
5. Catalysts for converting biomass into fuels and chemicals.

Our three-pronged strategy for technology transfer includes: cooperation agreements and licensing of on-demand technologies commissioned by industry; nucleation of spin-off companies; and extensive promotion of innovation and technology transfer, assisted by innovation agencies at UFSCar (www.inovacao.ufscar.br) and USP (www.inovacao.usp.br).

During the past four years, CeRTEV has maintained and expanded its extensive national and international industrial cooperation network. At present, approximately 10 such cooperation projects are active, with non-disclosure agreements (NDAs) or material transfer agreements (MTAs) signed and joint R&D projects being pursued. Despite the gloomy state of Brazil's national economy, some national companies have newly joined our network, providing funding for joint R&D projects. Industrial partners include Vetra, Nadir Figueiredo, SGD, Rhodia, and Alacer Biomedical (all from Brazil), Nippon Electric Glass (Japan), Nippon Sheet Glass (Japan), and Ivoclar-Vivadent (Liechtenstein). To intensify contacts with industrial clients, we recently established an Industrial Associates Group, mainly composed of members of the Commission on Glass of the Brazilian Ceramic Society (ABCeram) (http://abceram.org.br/membros-da-comissao). Overall, CeRTEV's industrial funding base, initially dominated by the glass armor and bioactive glass industrial sector, has diversified and now also includes contributions from companies interested in the mechanical, optical, and electrical properties of glasses and glass-ceramics.

A further significant highlight in the area of technology transfer has been creation of the first spin-off company from CeRTEV—VETRA High-TechCeramic Products was established in São Carlos by three CERTEV post-docs, based on their doctoral and post-doctoral research achievements. VETRA offers solutions for different market segments by developing glass and glass-ceramic materials that combine unique features, such as biodegradability, bioactivity, and bactericidal properties for biological applications, based on two recently granted international CeRTEV patents. Commercialization is supported by two Innovative Research in Small Business (PIPE/FAPESP) grants, entitled "Development of methodologies for the production of high purity bioactive glasses on industrial scale", and "Development of environmentally friendly cosmetics with bactericidal and healing effects for anti-acne application".

CeRTEV takes pride in its patent application record, with currently 12 patents in the area of glass synthesis and processing under examination at INPI (expected review period of 7–10 years) and one extended abroad. Technology transfer is also being promoted by various industrial workshops and discussion groups and the webpage Wikividros (https://wikividros.eesc.usp.br/), which is under construction and will serve as an open collaboration and discussion platform with partners and clients from industry.

4. Education and outreach

The CeRTEV Education and Outreach plan encompasses two strategic actions:

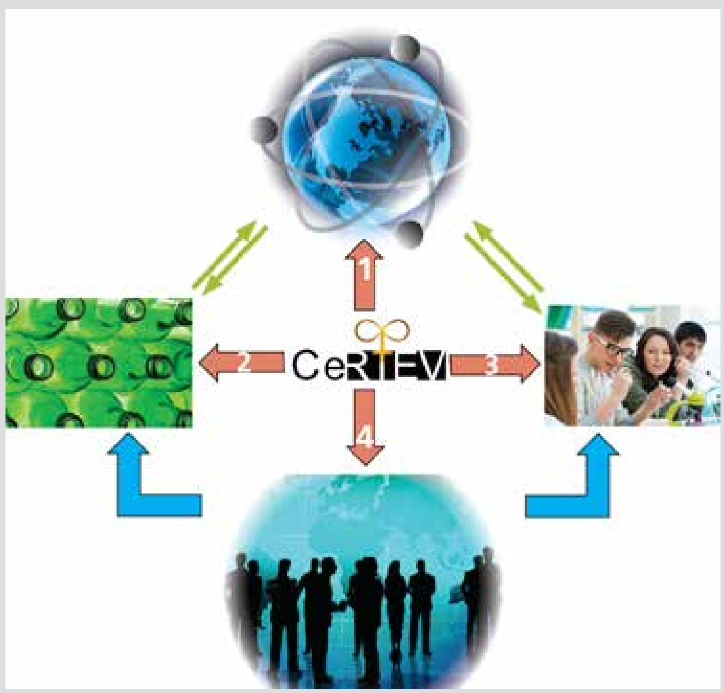
1. Developing and bolstering professional qualification in glass science and technology; and

2. Promoting glass as a very important and interesting material to both targeted audiences and the general public.

An important highlight has been the development of a technical course on glass science to train professionals for the glass industry, as presently there is no vocational training in this field in Brazil. Partnering with the Brazilian Association of Automated Glass Industries (ABIVIDRO) and the Paula Souza Center—the São Paulo state government office for technical education that manages 214 technical schools (ETECS) and 59 faculties of technology (FATECS) in 163 cities—we have developed a full curriculum for a three-semester glass technology course. The course consists of 450 hours of theoretical classes on glass formulation, physical processes, energy management, workplace and environmental safety, and entrepeneurship and 850 hours of practical training. Students may start specialization simultaneously with the second year of high school or at any time after completing high school. The course will be held in the city of Mogi das Cruzes (70 km from São Paulo), which holds one of the Paula Souza Technical Schools and also is the site of important Brazilian glass industries. The course is scheduled to start in the first half of 2018. For more information, visit www.cps.sp.gov.br/publicacoes/revista/2017/edicao-58-maio-junho.pdf.

A second education and outreach highlight has been the São Paulo Advanced School on Glasses and Glass-Ceramics, a nine-day workshop held at USP in August 2015 with approximately 100 highly qualified doctoral and masters students from 19 countries, including 35 participants from Brazil. The school covered state-of-the art topics on glass and glass-ceramics, including thermodynamics, crystallization, structure/property relations, and molecular dynamics simulations, and glass database manipulation delivered in 11 two-hour lectures and three tutorials. In addition, CeRTEV faculty guided groups of typically 4–5 participants to develop proposals for innovative research projects, which the students presented on the last day of the workshop. Based on highly positive evaluation feedback, we are confident that attendees benefitted greatly from this school and returned home with lots of inspiration and new ideas. We remain in contact with many of these future leaders in academic and industrial glass research and have already developed several collaborations and joint research projects with some of the participants and their advisors. For more information, visit www.ceramics.org/certev.

Aside from these highlights, CeRTEV members do their part to develop and present workshops in glass science and characterization within the professional community. These activities include a glass-ceramics internet course taught by Professor Zanotto in association



CeRTEV's scientific outreach activities are directed towards: (1) the science community, through conferences, workshops, and the School on Glass; (2) the glass industry, through a technical course on glass technology; (3) schools, through activities for the integration of education, research, and extension; and (4) the general public, through science dissemination in community educational events.

Students and lecturers from the São Paulo Advanced School on Glasses and Glass-Ceramics in front of the Laboratory of Vitreous Materials at the Federal University of São Carlos in Brazil.

with the International Materials Institute (IMI) (www.lehigh.edu/imi/teched/GlassProcess/Lectures/Lecture15_ZanottoA1.pdf). In addition, CeRTEV faculty have taught three short courses on fundamentals and applications of glass crystallization, at the GOMD-ACerS meetings in Miami (2015) and Madison (2016) and also jointly with IAB member Prof. A. Varshneya at SGT100 in Sheffield (2017). Finally, most of our glass classes are now available on YouTube at www.youtube.com/channel/UCvGLC2cszadfTXeLcyl_bVw.

CeRTEV has also mounted an extensive effort towards activities for the integration of education, research, and extension (ACIEPE), spearheaded by the UFSCar Rectorate, in which undergraduate students under the supervision of CeRTEV faculty have access to a public elementary school to discuss scientific topics. In a second step, involved elementary students (9–12 years old) visited the Laboratory of Vitreous Materials (LaMaV) at UFSCar, one of the main CeRTEV laboratories. During the past two years, we have reached out to approximately 400 students this way.

Additionally, a collaboration with the Ouroboros Group for the Dissemination of Science (www.facebook.com/ouroborosufscar) has helped reach hundreds of students through scientific shows on timely topics, including glass science, at various educational centers within a 500-km radius of CeRTEV. The Ouroboros group was also instrumental in developing CeRTEV's "Science on Stage" initiative of science dissemination through theater. Since 2014, approximately ten new plays on glass-related and other scientific topics have been developed and presented to more than 4,000 people at various academic and public events.

Related to this effort, glass musical instruments have been built to compose a small orchestra called "Vitreous Sounds". The line-up presently includes triangles, bassoons, berimbau, sweet, transverse and pan flutes, as well as carillon, quartz, kalimba, and organ of bowls, and it is being further expanded. Instruments are tuned with the aid of luthiers, glassmakers, and scientists. For more information, visit goo.gl/4uANhZ and goo.gl/X8Y3y8. Music from the glass orchestra also provides a background for about two dozen newly created one-minute radio presentations on glass topics, called "Vitreous Minute", that are broadcasted by local radio stations.

Further highlights of CeRTEV's outreach efforts include development of informative and creative printed materials and websites. In a two-month campaign, posters accompanied by an informative website were displayed in the São Paulo Metro system. Further, four "Vidro" comic book volumes (2,000 issues each) discussing the properties and curiosities associated with glass were produced and widely distributed to students (www.vidro.ufscar.br/#manga). Volume 1 deals with basic properties and the history of glass; Volume 2 discusses glass production and recycling; and Volumes 3 and 4 introduce optical fibers and bioactive glasses, respectively. We are currently creating Volume 5, entitled "The Glass Age."

It goes without saying that CeRTEV maintains a regular presence in major science fairs held in the state of São Paulo, having organized and/or participated in about a dozen such events during the past three years. In connection, we wish to highlight the itinerant exhibition "Glass World", which features experimental

The experimental "glass orchestra" of the Federal University of São Carlos in Brazil playing an opening show in December 2016.

demonstrations of properties and curiosities associated with vitreous materials, including light transmission by optical fiber, glass coloring by doping, acoustic properties, and photosensitive and flexible glasses. The interactive exhibition was presented at numerous major cultural events, reaching out to an audience of ~30,000 attendees.

5.Conclusions

During these first four years, we have consolidated a coherent collaborative research program dealing with fundamental research and development of new materials with technologically interesting properties, covering the full range of timely and potential application areas for glasses and glass-ceramics. Collaboration with partners in industry and extensive promotion of CeRTEV's research findings into marketable products is an integral part of our agenda, which also includes developing a new qualification channel for professionals in industrial glass and glass-ceramic sectors. Finally, our creative and highly diversified science dissemination program has already generated a tremendous amount of interest and positive feedback. Based on this three-pronged strategy, we hope to make more substantial contributions in the future to ensure sustained growth of the glass and glass-ceramic technology sectors in Brazil. For the seven years to come, our Center will cherish the opportunity to continue to lead Brazil's effort in glass science, technology, and education!

Covers of the first three volumes of Vidro, a series of comic books about glass.

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