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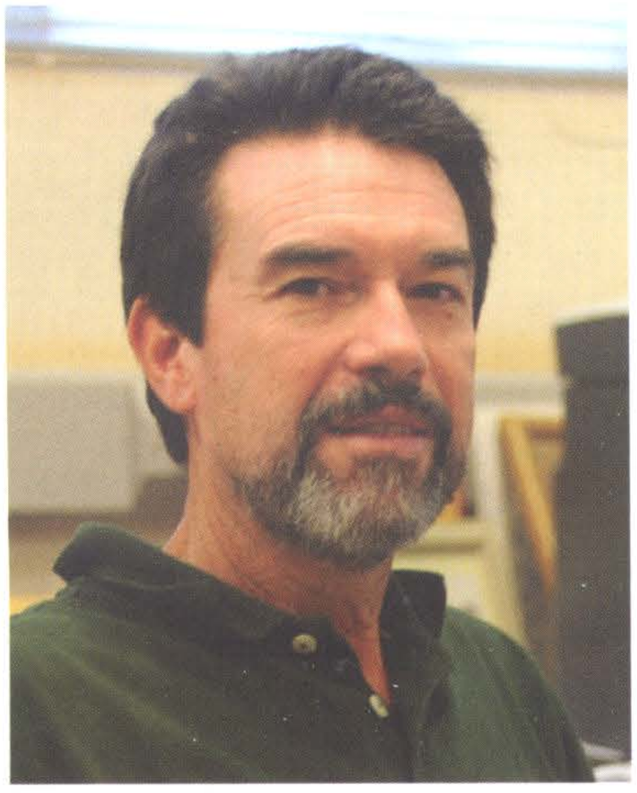
Vitreous materials research focus

Hellmut Eckert and Edgar D Zanotto discuss the history and present-day activities of the Sao Carlos Center of Research, Technology and Education in Vitreous Materials (CeRTEV) in Brazil. This multi-disciplinary centre unites the research groups of 14 professors in physics, chemistry and engineering.

Hellmut Eckert.



Edgar D Zanotto.

Four years ago, the Sao Carlos Center of Research, Technology and Education in Vitreous Materials (CeRTEV) was created with funds from the Sao Paulo Foundation (Fapesp) as part of the State's comprehensive CEPID programme. This multi-disciplinary centre unites the research groups of 14 professors in physics, chemistry and engineering at the Federal University of Sao Carlos (UFSCar), the University of Sao Paulo (USP) (both located in Sao Carlos) and the Sao Paulo State University (UNESP), located at Araraquara, 35km from Sao Carlos. They advise approximately 60 students and post-doctoral researchers and are embedded in a large Brazilian and international network of collaborations. Altogether, the centre, led by director Edgar D Zanotto is one of the largest academic 'glass' research teams on the planet.

CeRTEV's mission is to promote scientific, technological and economic progress in the area of glasses and glass-ceramics in the State of Sao Paulo and Brazil. The three pillars of this holistic effort are: State-of-the-art fundamental and applied research; development and promotion of new technology; and educational outreach to professionals, students and the general public. Its aim is to include Brazil in the ranking of the world's top 10 glass research and technology countries and to foster the economic development and growth of the productive glass sector in Brazil.

CeRTEV reports on a yearly schedule to its main sponsor (Fapesp) and to 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 the scientific agenda and about half of all board members have become collaborators in the meantime. In 2015, CeRTEV obtained excellent marks in an interim evaluation conducted by an international group of referees appointed by Fapesp.

RESEARCH AGENDA AND PROGRESS

The 14 groups have consolidated a coherent research agenda, developing glasses and glass-ceramics with important functionalities, such as high mechanical strength, electrical conductivity, biological, optical or catalytic activity and/or combinations of these properties. Work is being carried out in five core areas: Structural materials for architecture and construction, armour, as well as dental restoration; bioactive glasses and glass-ceramics for bone and cartilage healing and growth; ion-conducting materials for applications in modern battery technologies; photonic glasses and glass-ceramics for lasers and optical sensors; and catalytically-active systems. These areas reflect the enormous importance of glassy materials in meeting future societies' needs for improved safety, health, communication, energy management and environmental protection, as modern society has entered the 'glass age'.

As technology developments and fundamental scientific insights are truly inseparable in this field, a few directions and highlights of CeRTEV's research programme are highlighted here. In its research effort on structural materials, the organisation has uncovered the mechanistic principles for the toughening process in lithium disilicate glass-ceramic - crack deflection, crack bowing and trapping and crack bridging. Theoretical models for the elastic modulus, crystal fracture toughness and crystallised volume fraction have been developed and successfully tested to explain the increased fracture toughness with increased crystallised volume fraction for the full range of crystallisation in glass-ceramics of this composition. Using spectroscopic methods, researchers are currently trying to understand mechanical properties on the basis of structure and dynamics on different scales of length and time.

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 innovative bioactive formulations and composites, such as Biosilicate for applications in bone repair and dental restoration. Recent histopathological, cytotoxicity and genotoxicity analyses have confirmed that Biosilicate scaffolds possess excellent biocompatibility. Researchers are further continuing to explore compositional effects on various aspects of bioactivity performance, by substituting calcium with magnesium or strontium and by developing boron-containing bioactive glasses.

Glass-ceramics based on lithium titanium (or germanium) phosphate compositions featuring highly mobile alkaline ions have shown significant promise for applications as solid electrolytes in high energy storage devices. CeRTEV researchers are trying to better understand the composition/structure/performance relationships in these systems. Modern solid-state NMR techniques have provided valuable insight to the influence of the crystalline fraction on the ionic mobility and electrical conductivity. Investigations are now gradually shifting from lithium towards sodium-based glass-ceramics because sodium features similar electrochemistry as lithium but is much more abundant than the latter.

CeRTEV's activities in the area of photonic glasses and >

Optical micrograph showing a plethora of lithium metasilicate crystals embedded in the residual matrix of a rare (nucleant-free) glass-ceramic. The bar indicates 100 micrometers.

glass-ceramics are focusing on the development and characterisation of 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 ion species in fluoride phosphate matrices have been studied by recently developed NMR and EPR approaches, leading to an understanding of their photophysical characteristics regarding the ligand distribution around the rare earth ion species.

Researchers will now proceed to the second step of preparing glass-ceramics, based on rare-earth-doped fluoride nanocrystals embedded in a glassy environment. They also co-dope these glasses with metallic nanoparticles to enhance the luminescent properties via surface plasmon resonance effects.

Another area of active research within CeRTEV is the development of photonic inorganic-organic hybrid materials and nanocomposites. Besides offering the possibility of designing a more favourable chemical environment to improve the photophysical properties of the guest molecules, encapsulation in these solids also protects the emitter molecules, prevents their leakage (especially critical for biological applications) and ultimately leads to more robust and versatile materials.

An entirely new application field of glass-ceramics is being developed in the fifth topical CeRTEV research area, devoted to catalytically active systems for the conversion of biomass to fuel and fine chemicals. These materials are hierarchically structured, combining mesoporosity (for catalytic conversions) with macroporosity (for facilitating mass transport of highly polymerised substrates). Techniques under development include ceramic foaming based on the use of porogenic agents, selective leaching of phase-separated base glasses and template sol-gel synthesis using molecular precursors.

In pursuing its research agenda, CeRTEV has been reaping the synergetic benefits from results obtained in these different application areas. It has already developed various excellent glass and glass-ceramic systems, whose technological application potential is being explored together with industry partners.

INNOVATION AND KNOWLEDGE TRANSFER

CeRTEV activities are channeled towards the generation of technologies and patents, all the way to new products and production processes (a 'science to business' approach). Thus far, new or improved patentable glass or glass-ceramic materials have been developed for light armours (for use in aircraft, cars and for individuals), tougher monolithic glass-ceramics for dental restoration, macroporous and hierarchically ordered scaffolds, fibres, small monolithic parts and powders with increased osteoinductive activities, combined with the ability for targeted drug delivery for bone and tissue repair.

A three-pronged strategy for technology transfer includes co-operation agreements and licensing of on-demand technologies commissioned by industry, nucleation of spin-off companies and extensive promotion of innovation and technology transfer.

During the past four years, CeRTEV has maintained and expanded its extensive national and international industrial co-operation network. At present, eight such co-operation projects are active, with non-disclosure agreements (NDAs) and material transfer agreements (MTA) signed and with joint R&D projects being pursued. Despite the gloomy state of Brazil's national economy, several local companies have recently joined the network, providing funding for jointly pursued R&D projects. Industrial partners include Vetra, Nadir Figueiredo, SGD, Rhodia, Alacer Biomedical, Nippon Electric Glass, Nippon Sheet Glass and Ivoclar-Vivadent. To intensify contact with industrial clients, an Industrial Associates Group has been established, composed mainly of members of the Commission on Glass of the Brazilian Ceramic Society (http://abceram.org.br/membros-da-comissao).

A further significant highlight in the area of technology transfer has been the creation of the first spin-off company from CeRTEV: VETRA High-Tech Ceramic Products was established in Sao Carlos by three CERTEV post-docs, based on their doctoral and post-doctoral research achievements. It offers solutions for different market segments by developing glass and glass-ceramic materials that combine individual features, such as biodegradability, bioactivity and bactericidal properties for bio-applications, based on two recently granted international CeRTEV patents. Commercialisation is supported by the two Innovative Research in Small Business (PIPE/FAPESP) grants. They concern applications of a boron-containing >

bioactive glass formulation called 'F18' (the 18th composition developed in an iterative optimisation process), allowing the fabrication of continuous glass fibre for long periods of time via large-scale processing techniques, such as downdrawing. Besides bioactivity and high reactivity, F18 also presents a remarkable bactericidal effect, a highly desired property. The F18 development opens avenues in tissue engineering and the 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 some clinical applications.

CeRTEV takes pride in its extensive patent application record, with 12 patents in the area of glass synthesis and processing currently under examination. Technology transfer is also being promoted by various industrial workshops and discussion groups and the development of the webpage Wikividros; https://wikividros.eesc.usp.br/ (under construction), to serve as an open collaboration and discussion platform with partners and clients from industry.

EDUCATION AND OUTREACH

CeRTEV's education and outreach strategies focus on the development of long-term sustainability of glass science and technology in Brazil. At present, the national glass industry faces a serious shortage of qualified technical personnel. This problem arises from a complete lack of technical training courses dedicated to professionals in this area.

Therefore, together with its partner ABIVIDRO, (Brazilian Association of Automated Glass Industry) and the Paulo Souza Center, a Sao Paulo State Government office that now administers 214 technical schools and 59 faculties of technology in 163 municipalities, CeRTEV has developed a full curriculum for a three-semester course. The course includes 450 hours of theoretical training in glass formulation, physical processes, energy management, workplace and environmental safety and entrepreneurship and 850 hours of practical operations. Students can start this specialisation in parallel to the second year of high school or at any time if they have completed high school. The course will be held in the city of Mogi das Cruzes (70km from the city of Sao Paulo), which is the site of an important Brazilian glass industry, Nadir Figueiredo and which holds one of the technical schools from Paula Souza Center. The course is scheduled to commence in the first semester of 2018. See also http://www.cps.sp.gov.br/publicacoes/revista/2017/edicao-58-maio-junho.pdf.

Aside from these highlights, CeRTEV members do their part in developing and presenting workshops in glass science and characterisation within the professional community. These activities include a glass-ceramics internet course taught by Professor Zanotto, in association with the International Materials Institute (IMI), see http://www.lehigh.edu/imi/teched/GlassProcess/Lectures/Lecture15_ZanottoA1.pdf. Finally, most glass classes are now available on youtube: https://www.youtube.com/watch?v=6U0IIodQujs&list=PLYkqBrOsu1yCxMLTcb7Y6zwj_smIb5w5x and :https://www.youtube.com/watch?v=AB9H6v3Ctew&list=PLYkqBrOsu1yA2K5wQZjn1WSs8U7BtJ-5.

In parallel, an aggressive effort has been mounted, promoting the importance of glass and glass-ceramics to the public. As part of UFSCar's ACIEPE initiative (activities for the integration of education, research and extension) the organisation has been able to reach out to approximately 400 students from elementary schools, making classroom presentations and inviting students to its university laboratory. Also, collaboration with the Ouroboros Group for the Dissemination of Science has helped CeRTEV to reach out to hundreds of students with presentations of timely scientific topics (including glass science) at various educational centres within a 500km radius.

The Ouroboros group was also instrumental in developing CeRTEV's Science on Stage initiative of science dissemination through theatre. Since 2014, approximately 10 plays on glass-related and other science topics have been developed and presented to more than 4000 people at various academic and public events. Related to this effort, glass musical instruments have been built to create an orchestra (Vitreous Sounds). The line-up presently includes triangles, bassoons, berimbau, sweet, transverse and pan flutes, as well as carillon, quartz, kalimba and the organ of bowls and is being expanded further. Instruments are tuned with the aid of luthiers, glassmakers and scientists. See http://g1.globo.com/sp/sao-carlos-regiao/jornal-da-eptv-2edicao//videos/v/ufscar-tem-orquestra-com-instrumentos-feitos-de-vidro-no-laboratorio-de-quimica/5563158/andhttp://g1.globo.com/sp/sao-carlos-regiao/bom-dia-cidade/videos/v/orquestra-de-vidro-da-ufscar-se-apresenta-pela-1a-vez/5517562/. Music from the glass orchestra also provides the background for about two dozen recently created one minute radio presentations on the topic of glass (Vitreous Minute) broadcast by local radio stations.

Further highlights of CeRTEV's outreach effort include the development of informative and creative printed material and websites. In a two month campaign, three posters, accompanied by an informative website were displayed in the Sao Paulo Metro system. Furthermore, four comic book volumes (2000 issues each) discussing the properties and curiosities associated with 'glass' were produced and widely distributed to students, see http://www.vidro.ufscar.br/#manga. Volume one deals with basic properties and the history of glass. Volume two is about glass production and recycling, while volumes three and four introduce optical fibres and bioactive glasses. A fifth volume, entitled 'The Glass Age' is in progress.

Finally, the itinerant Exhibition 'Glass World' can be higlighted, which features experimental demonstrations of properties and curiosities associated with vitreous materials, including light transmission by optical fibre, glass colouring by doping, acoustic properties, photosensitive and flexible glasses; see http://g1.globo.com/sp/sao-carlos-regiao/jornal-da-eptv-2edicao//videos/v/ufscar-tem-orquestra-com-instrumentos-feitos-de-vidro-no-laboratorio-de-quimica/5563158/. The interactive exhibition was presented at numerous major science fairs and other cultural events, reaching out to a total audience of about 30,000 attendees.

CONCLUSIONS

In summary, during the first four years, a coherent, collaborative research programme has been developed, dealing with fundamental research and the development of new technological materials, covering a broad range of important 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 the strategy, which also includes increasing the supply of qualified professionals in the productive glass and glass-ceramic sector.

As the creative and highly diversified educational outreach programme has already generated a tremendous amount of interest and positive feedback, the authors are optimistic that CeRTEV will be attracting more talented and skilled individuals to this important area of modern society's technological and economic future. For the seven years to come, the centre will cherish the opportunity of continuing to collaborate with industries in challenging, relevant problems and to lead Brazil's effort in glass science, technology and education.

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