CeRTEV – Center for Research Technology and Education in Vitreous Materials

Report of Activities – 4th year[1]

Period covered by this report: 2 years - July 2015 – July 2017

Contents[2]

1. RIDC Identification[9] **(max. 2 pages)**

RIDC: CeRTEV – Center for Research Technology and Education in Vitreous Materials

The core group of the Center comprises 13 professors at USP and UFSCar (both located in São Carlos) and 1 at UNESP (located 35 km from São Carlos) who are experts in engineering, chemistry and physics of vitreous materials, including glass structure characterization, crystallization kinetics and properties, and a wide range of structural and functional characterization 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. This is one of the smallest group among the 17 FAPESP funded research centers (CEPIDs) in the State of São Paulo, and yet one of the **largest academic "glass" research** teams in the world! We

[1] Este relatório deve procurar sumarizar e salientar as atividades do Cepid no período 2015-2017, enfatizando pontos importantes de suas atividades e resultados. Ele será encaminhado ao Comitê Internacional que assessora a FAPESP nas avaliações periódicas dos Centros, juntamente com os relatórios anuais.
[2] Para facilitar o manuseio do relatório, por favor, organize um índice com as respectivas páginas de cada tópico.
[3] Identificação do centro e de suas lideranças, conforme previsto no Edital 2011.
[4] Resumir os resultados de transferência de conhecimento (incluindo, mas não limitado a tecnologia, patentes, software, bases de dados, produtos, políticas públicas e outros). Deve-se também indicar o link para a página de resultados de Propriedade Intelectual do Centro, conforme o email enviado aos Cepids em 26/10/2016).
[5] Lista de financiamentos obtidos pelo Centro de fontes outras, excluindo a FAPESP. Deve-se incluir salários de docentes e servidores diretamente ligados ao Centro, como técnicos e apoio administrativo, e demais despesas custeadas pelas respectivas universidades. A tabela deve ser preenchida com o montante total recebido no período. Exemplos: 1) somar todas as bolsas e período total: uma bolsa PD - CNPq, doze meses (valor da bolsa X 12) + cinco bolsas PD – CAPES, 24 meses (5X valor da bolsa X 24); 2) somar os montante efetivamente gastos de recursos de outras agências como edital Universal CNPq + montante efetivamente gasto de recursos FINEP + INCT, etc); 3) somar os salários dos pesquisadores principais e associados dedicados ao CEPID no período de dois anos cobertos pelo relatório; 4) somar os salários dos funcionários técnicos e administrativos dedicados ao CEPID no período de dois anos cobertos pelo relatório. Apoios efetivamente gastos em moeda estrangeira deverão usar a cotação de R$ 3,2 para conversão do dólar.
[6] Além dos valores financeiros/econômicos indicados no quadro acima, incluir informações que julgar pertinentes envolvendo a contrapartida institucional. Eventuais dificuldades também devem ser aqui reportadas.
[7] URL das publicações do CEPID no *MyResearcherID* e no *Google Scholar*, conforme definido na avaliação de 2015 e reafirmado no e-mail aos Cepids de 26/10/2016. Em cada uma delas, listar todas as publicações resultantes de pesquisas realizadas pelo Centro apenas do período de vigência do CEPID, ou seja, a partir de 2013. Pode-se incluir uma lista de produção de resultados que eventualmente não constem das duas páginas, se julgar relevante.
[8] Por gentileza, anexe todos os relatórios e documentos produzidos pelo Conselho Consultivo Internacional do Cepid (*International Advisory Board*), devidamente identificados com número, data e autoria. Na página do Cepid sob sua responsabilidade, deve ser criado um espaço, acessível mediante senha, com todas essas informações.
[9] Identificação do centro e de suas lideranças, conforme previsto no Edital 2011.

are researching and developing new glasses and glass-ceramics presenting application-relevant functionalities, such as high mechanical strength and electrical conductivity, biological, optical or catalytic activity, and/or combinations of these properties. A fundamental understanding of these properties is sought on the basis of the structural organization of these materials on different length scales.

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Host institution: Federal University of São Carlos

Associated institutions: University of São Paulo – São Carlos, University State of São Paulo - Araraquara

Webpage: www.certev.ufscar.br

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2. Scientific Report (max. 8 pages)

2.1- RIDC Mission

The CeRTEV comprises 14 investigators and their co-workers who advise about 60 graduate students and post-docs. Pursuing the objectives of the CEPID program of the State of São Paulo, CeRTEV's **mission** is to conduct state-of-the art ***research***, ***technology*** development, and ***education*** and outreach in the area of Glasses and Glass-Ceramics. We aim to include Brazil in the ranking of the top glass research countries in the world.

As part of the joint CeRTEV research agenda, the 14 research groups work together to develop new glasses and glass-ceramics, presenting application-relevant functionalities such as high mechanical strength, electrical conductivity, biological, optical or catalytic activity, and/or combinations of these properties. CeRTEV's agenda is sub-divided into core areas, dedicated to the five principal application fields of glasses and glass-ceramics: (1) ***structural materials*** for architecture and construction, armor, as well as 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 fundamental research encompassing the development of general concepts regarding the structural description of glasses and the structural, dynamic (diffusion, relaxation and viscous flow) and mechanistic aspects of the nucleation and crystal growth processes involved in the crystallization of glasses

leading to glass-ceramics. A brief summary of the research highlights is given further below; more detail can be found in the annual scientific reports.

On the technology side, CeRTEV activities are channeled towards the generation of new technologies and patents, all the way to new products and production processes ("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, cars and individuals), 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 the other CeRTEV research areas are underway.

CeRTEV's education and outreach strategies focus on the development of long-term sustainability of glass science and technology in Brazil. At the present time, the complete lack of training courses dedicated to professionals in the glass industry seriously impinges upon its development. To remedy this situation, we have developed a comprehensive curriculum for a new technical course in cooperation with two professional organizations, the ABIVIDRO and the Paula Souza Center, which will result in trained professionals for the glass industry. In parallel we have mounted a concerted effort promoting the importance of glass and glass-ceramics to the public. Our educational activities include the 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 ("science on stage").

2.2- Executive summary [10]

During the past two years CeRTEV scientists have published about 90 indexed scientific papers on glasses and vitreous materials. This accounts for approximately 20% of all inorganic glass research papers by Brazilian institutions. Several patents have been filed in the area of functional glasses and glass-ceramics. The CeRTEV coordinator, Professor Zanotto was honored in 2016 by the Materials Research Society of India (MRSI), which created the "*ED Zanotto Award*" for glass science. Zanotto serves as one of the three Editors for the "Journal of Non-Crystalline Solids". Professor Hellmut Eckert, CeRTEV`s vice coordinator, was honored in 2016 with the prestigious G.W. Morey award for excellence in glass research by the GOMD of the American Ceramic Society. Until December 2016, he served as the Editor-in-chief of the journal "Solid State Nuclear Magnetic Resonance". CeRTEV has exercised further international scientific leadership by organizing the ***São Paulo Advanced School on Glasses and Glass-ceramics*** (with about 65 top international PhD students from 19 countries and 35 Brazilian PhD students) during August 1-9, 2015, and co-organizing in 2016 a ***Crystallization Symposium*** in Madison, USA, the ***Don Uhlmann Festschrift*** in Madison, USA, and the ***Larry Hench Honorary Symposium*** in Sheffield, UK. They also co-organized the ***XI Brazilian Symposium on Glass and Related Materials***, to be held in Curitiba in July 2017. Another important sign of CeRTEV´s reputation is that among 10 important glass congresses organized worldwide in 2017, CeRTEV faculty delivered (or will deliver) invited and plenary talks in **7**

[10] Sumário executivo das atividades realizadas, nos últimos dois anos (julho de 2015 a julho de 2017), pelo CEPID, indicando o desenvolvimento da pesquisa desde a última avaliação, as metas atingidas e/ou superadas, bem como objetivos que eventualmente demandem revisão. É importante salientar as iniciativas e resultados associados aos pontos levantados na última avaliação do Cepid pelo Comitê Internacional, em 2015 (e discutidos no documento Reply and Actions 2016).

(Kolkata-India, Nagaoka-Japan, Kona-USA, Curitiba-Brazil, Sophia-Bulgaria, Segovia-Spain, Pittsburgh-USA). Finally, CeRTEV faculty delivered 2 of the 3 most prestigious international glass science "lectures": the Turner Memorial Lecture during the centennial of the Society of Glass Technology, UK, in 2016 and the GOMD´s A. Cooper Distinguished Lecture in 2017.

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 During the past two years, CeRTEV's research progress has been communicated and discussed in three board meetings: May 2015 (Miami), May 2016 (Madison) and July 2017 (Curitiba, Brazil). Valuable recommendations from the ***IAB*** have been added regularly to complement our scientific agenda. Their evaluation reports can be seen at CeRTEV´s website. Finally, IAB members **Boccaccini, Brow, Jain and Glebov were granted very prestigious glass science and technology awards and lectures in this period**!

A top priority for CeRTEV's success is the development of a coherent research program aligning the activities of its individual members with the 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. Below we describe the main lines of our joint research, highlight some key results, and indicate further directions to be pursued within the next funding period.

An important example of collaborative synergy within CeRTEV has been the incorporation of solid state NMR spectroscopic methods for studying structure/property correlations in functional glasses and glass ceramics and in elucidating the structural aspects of nucleation mechanisms. While the vast majority of glass forming substances only undergoes surface (heterogeneous) nucleation when sufficiently heated, a few systems also show the thermodynamically less favorable case of internal (homogeneous) nucleation on laboratory time/length scales. Results obtained by advanced solid state NMR techniques suggest a positive correlation between homogeneous nucleation ability and structural similarity at the level of short- and intermediate range order, particularly with regard to the arrangement of the network modifier cations. For understanding nucleation and crystallization processes, molecular dynamics simulations are by now also becoming an increasingly important part of our research agenda, enhancing our understanding about diffusion mechanisms, relaxation processes and dynamical heterogeneities in glass-forming liquids. The development of improved interaction potentials for homogeneously nucleating liquids is an essential part of this effort. On the experimental side, we are continuing our development of new differential scanning calorimetry (DSC) approaches, advanced solid state magnetic resonance methodology and Raman spectroscopic investigations for studying structure/property relations in glasses, as well as crystal nucleation and growth during the formation of glass-ceramics.

In our research effort on ***structural materials,*** new mechanistic concepts for the toughening process in lithium disilicate glass-ceramic - crack deflection, crack bowing and trapping, and crack bridging have been developed. A model incorporating the elastic modulus, crystal fracture toughness and crystallized volume fraction was proposed and successfully tested to explain the increased fracture toughness with crystallized volume fraction for the full range of crystallization in glass-ceramics of this composition. Using spectroscopic methods we are continuing our investigations to develop a foundation of this model on the basis of structural and dynamic details 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 new 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. These materials have also been successfully introduced as new additives to calcium phosphate cements (CPCs), which are used as an alternative to biological grafts due to their excellent osteoconductive properties. We are further continuing to explore compositional effects on various aspects of bioactivity performance, in particular with regard to the substitution of Calcium by Magnesium or Strontium, and the examination of boron-containing bioactive glasses.

Glass-ceramics based on lithium titanium (or germanium) phosphate compositions crystallizing in the NASICON structure have shown significant promise for applications as ***solid electrolytes*** in high energy storage devices. The CeRTEV research agenda focuses on enhancing the understanding of composition/structure/performance relationships in these systems. Modern solid state NMR techniques have provided important insight into the influence of the crystalline fraction on the ionic mobility and electrical conductivity. Our investigations are now gradually shifting towards sodium-based glass-ceramics (NTP), because sodium features similar electrochemistry as lithium but is much more abundant than the latter. Along similar lines, we will also explore oxy-chalcogenide glass compositions forming superionic crystals upon ceramization.

CeRTEV's activities in the area of ***photonic glasses and ceramics*** are focusing on the 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 ion 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 the ligand distribution around the rare earth ion species. We will now proceed to the second step of preparing glass-ceramics, based on rare-earth doped fluoride nanocrystals embedded in a glassy environment. Current work focuses on co-doping these glasses with metallic nanoparticles that can potentially enhance the luminescent properties of dopant ions, due to interaction via surface plasmon resonance. The efficiency of this process is highly dependent on the size of the metallic nanoparticles, whose control is under active investigation. These studies have benefitted greatly from introducing advanced electron paramagnetic resonance techniques. We are also currently applying these methods to understand the initial stages of crystallization in photothermal refractive (PTR) glasses. Another area of active research within CeRTEV is the 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 the guest molecules, encapsulation in the solids also protects such 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 polymerized substrates). Techniques under development include (a) ceramic foaming based on the use of porogenic agents, (b) selective leaching of phase-separated base glasses, and (c) sol-gel techniques using molecular precursors. Catalytic functionalization with niobium or vanadium oxyphosphates is done either by grafting the internal surfaces with suitable precursors or by incorporating the active species already in the synthesis formulation. The catalytic performance of these materials is currently being tested in the batch mode using the cellulose-hydroxymethyl furfural model reaction.

In summary, we have developed the full range of activities in all of the areas delineated in the original CeRTEV proposal, and we have been reaping the synergetic benefits from results obtained in these different application areas. We anticipate that as the result of our research efforts we will soon have various excellent glass and glass-ceramic systems available for which technological application potentials can be further studied in conjunction with our partners in industry.

2.3 – Research Results Highlights

Summary 2013- (May) 2017:

Glass structure and crystallization:	28 papers
Special techniques	12
Strong glass-ceramics	05
Bioactive glasses and glass-ceramic	31
Energy storage/electrical properties	24
Photonic materials	45
Catalytic systems	09

Total number of publications on glass and related materials: 154 (about 11 per member, 17 per PI)
Papers with collaboration within CeRTEV: 52 (34%)
Papers with international collaborators: 42 (27%)

2.3.1 - RIDC Main Accomplishments[11]

2.3.1.1. Fundamentals of crystal nucleation and growth in glasses.

New fundamental insights into 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 glass – 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 the critical crystalline nuclei, and can perhaps explain the often reported breakdown of the 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 the heterogeneous one only in those glasses in which the short and medium-range order of the network modifier species in the glassy phase closely resembles that of the isochemical material crystallizing from it [3].

[11] Research Results Highlights é uma seção que deve conter uma lista curta de (5 a 10) itens de destaques de pesquisa. Essa lista deve permitir ao leitor identificar os principais avanços obtidos pelo Centro no período relativo ao relatório. Os destaques da pesquisa, como a demonstração de um teorema, a descoberta de um gene ou o desenvolvimento de um medicamento, por exemplo, devem ser aqui explicitados. Os trabalhos publicados e outras produções associadas aos Resultados de Pesquisa selecionados devem ser claramente citados e incluídos como lista da Seção 2.3.2.

2.3.1.2. Structure-Dynamics-Property Relationships.

Structure-Property relations have been examined, over the full range of length scales (μm to Angstroms) in all of CeRTEV's topical areas. We found that the strength and toughness of lithium disilicate (LS_2) armor 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 the 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, the emission characteristics of photonic glasses can be understood on the basis of the direct atomic environments of the active rare earth (RE) dopant ions, as revealed by correlated NMR, EPR and Raman spectroscopic results [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].

2.3.1.3. Strong Glasses and Glass-Ceramics for Armor Applications

Aside from the above-mentioned fundamental work on LS_2 armor ceramics [4], further highlights in this area include the development of new formulations for multiphase glass- ceramics and the characterization of their extremely promising mechanical stabilities. We developed a brand new (difficult to make) transparent magnesium aluminosilicate glass-ceramic intended for armor applications, and evaluated its elastic properties at low and high temperatures. The results of the first ballistic tests are very promising [8]. We also studied homogeneous crystallization of a new series of lithium calcium silicate glasses in the absence of nucleation agents [8]. 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 glass-ceramic with outstanding mechanical properties for load bearing applications [9].

2.3.1.4. Bioactive Glasses and Glass-Ceramics

CeRTEV's outstanding highlight in the area of bioactive glasses has been the development of a new glass formulation ("F18"), allowing the fabrication of continuous glass fiber for long periods of time via large scale processing techniques, such as downdrawing [10]. Besides bioactivity and high reactivity, F18 also presents a remarkable bactericidal effect, a highly desired property. The F18 development opens new venues in tissue engineering and in 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 a number of clinical applications [10]. Further studies at CeRTEV have focused on widening the clinical application portfolio of Biosilicate®, a fully crystalline osteo-inductive glass-ceramic [11] for bone and tissue repair [11, 12]. Detailed mechanistic studies show that Biosilicate affects the osteoblast's expression of genes associated with the process of mineralization highlighting their osteostimulation property [13].

2.3.1.5. Fast Ion Conducting Glasses and Glass-Ceramics.

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 iso- and aliovalent substitution strategies, we have contributed new homogeneously crystallizing formulations with competitive ionic conductivities [14, 15]. Currently we are developing glass-ceramic routes for the preparation of sodium-containing superionic conducting materials. This work is motivated by the 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 the cationic or the anionic sublattices [16], leading to significantly enhanced ionic conductivities.

2.3.1.6. Photonic Glasses and Glass-Ceramics

New rare-earth doped glass formulations based on fluorophosphate and -tellurite matrices have been developed for laser applications and white-light generation. The radiative properties of these materials are comparable to the best results currently available in the literature [17]. 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 [18]. 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 [19], on the growth kinetics of these nanoparticles by in-situ monitoring [20], on intriguing valence changes upon the ceramization of heavy metal oxide glasses [21], and on the photo-ionization process in photothermal refractive (PTR) glasses [22].

2.3.2. Corresponding published works (CeRTEV researchers in **bold**)

[1] **E.D. Zanotto**, D.R. Cassar, D.R., *Sci. Rep*. 7 (2017), 43022.
[2] P.K Gupta, D. R. Cassar, **E. D. Zanotto**, *J. Chem. Phys.* 145 (2016), 211920.
[3] **E. D. Zanotto**, Tsuchida, J.E., **J. F. Schneider, H. Eckert**, *Int. Mater. Rev.* 60 (2015), 376-391.
[4] F. C. Serbena, I Mathias, C: E. Foerster, **E. D. Zanotto,** *Acta Materialia.* 86 (2015), 216.
[5] **H. Eckert,** *Diffusion Foundations*, H. Mehrer, ed., Trans Tech. Publ. Vol. 6, 144-193 (2016).
[6] M. de Oliveira Jr, T. S. Gonçalves, C. Ferrari, **C. J. Magon, P.S. Pizani, A.S.S.de Camargo, H. Eckert,** *J. Phys. Chem. C*121 (2017**)** 2968-2986.
[7] Rodrigues, A. M.; **Rino, J. P.; Pizani. P.S.**; **Zanotto, E. D.**, *J. Phys. D: Appl. Phys* 49 (2016),435301/1-10
[8] L. Sant'Ana Gallo, F. Célarié, N. Audebrand, **A. C. M. Rodrigues, E.D. Zanotto,** T. Rouxel, *J. Am. Ceram. Soc.*, 2017, in press
[9] G. G. Santos, F. C. Serbena, V. M. Fokin**, E. D. Zanotto,** *Acta Materialia* 2017, in press
[10] M. T. Souza, O-**Peitl, E. D. Zanotto,** BR 102013020961 9 (August 2013), PCT: BR2014/000275 (Feb. 2015), USPTO - US 14/911,444 (granted)
[11] M.C. Crovace, M. T. Souza, C. R. Chinaglia, **O. Peitl Filho, E.D. Zanotto, E.D.** *J. Non-Cryst. Solids*, 432 (2016), 90-110.
[12] C. I. A. van Houdt, C.R. Tim, M. C. Crovace, **E.D**.**Zanotto, O. Peitl Filho,** D. J. O.Ulrich, J. A. Jansen, N. A. Parizotto, A. C. Renno, J. J. J. P van den Beucken, *Biomed. Mater*.10(2015) 035003
[13] E. P. Ferraz, F. S. Oliveira, P. T. Oliveira, M. C. Crovace, **O. Peitl Filho**, M. M. Beloti, A. L. Rosa, *J. Biomed. Mater. Res. A*, v. 105 (2017), 419-423.
[14] S. Santagneli, H. Baldacim, S. J. L. Ribeiro, S. Kundu, **A. C. M. Rodrigues**, C. Doerenkamp, **H. Eckert**, *J. Phys. Chem C*, 120 (2016), 14556- 14567.
[15] R.B. Nuernberg, **A.C.M. Rodrigues,** *Solid State Ionics* 301 (2017) 1-9.
[16] S. Kundu, H. Bradtmüller, **H. Eckert**; **A.C.M. Rodrigues,** to be published.

[17] T. S. Gonçalves, R. J. Moreira Silva, M. de Oliveira Jr., C. R. Ferrari, G. Y. Poirier, **H. Eckert**, **A. S. S. de Camargo**, *Mater. Chem. Phys.* 157 (2015) 45-55.
[18] R. Dagupati, M. Reza Dousti, Raja J. Amjad, **A. S. S. de Camargo**, *J. Non-Cryst. Solids* 450 (2016) 149-155.
[19] D. Rajesh, R. J. Amjad, M. R. Dousti, **A. S. S. de Camargo**, *J. Alloys Comp*. 695 (2017) 607-612.
[20] **M. Nalin,** R. S. Manzan, **J. P. Donoso, C. J. Magon**, A. Tercjak, C. Rüssel, to be published.
[21]V. Volpi, M. Montesso. S. J. L. Ribeiro, W. R.Viali, **C. J. Magon,** I. D. A**.** Silva, I. D. A.; **J. P. Donoso, M. Nalin, M.***J. Non-Cryst. Solids*431 (2016)135-139.
[22] **C. J. Magon, J. P. Donoso,** F.de Lima, **H. Eckert, E. D. Zanotto**, J. Lumeau, L. Glebova, L.Glebov, *J. Non-Cryst. Solids452* (2016) 320-324.

3. Innovation and Knowledge Transfer Report[12] (max. 2 pages)

CeRTEV's research achievements are continuously being channeled into innovation, all the way from new technologies and patents, to new products and processes (*science to business approach*). This agenda encompasses all the application fields of our research agenda, i.e. 1) strong GCs 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 ***(a) cooperation agreements and licensing of on-demand technologies commissioned by industry***, ***(b) nucleation of spin-off companies*** *and* ***(c) extensive promotion of innovation and technology transfer,*** assisted by the 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 15 such cooperation projects are active, with non-disclosure agreements (NDAs) signed and joint R&D projects being pursued. Despite the gloomy state of Brazil's national economy, several national companies have newly joined our network, providing generous funding for jointly pursued R&D projects. Industrial funding contributors in the period include ***Nadir Figueiredo*** – Consulting about glass kitchen ware (Ana Rodrigues), ***SGD*** – *perfume container glasses* (Nalin), ***Rhodia*** *–Biomass for glass preparation* (Bellini Ferreira), ***Alacer Biomedical*** *– Development of solid-state pH sensors. (*Andreeta), ***Owens Illinois –*** *Member of TAB, Largest Glass Bottle Producer in the world* (Zanotto), and ***Nippon Electric Glass*** – *Structure-Property Correlations in Scratch Resistant Glasses* (Eckert), ***Ivoclar*** – *Development of a new, strong dental glass-ceramic*, NDA and MTA (Material Transfer Agreement) signed (Zanotto). Finally, ***Serrapilheira Institute*** (defined below) is funding 2 research projects at UFSCar (Zanotto). During the review period 2015-2017 all of our industrial clients and cooperation partners contributed with R&D support in the amount of approximately R$ 900.000. To intensify contacts with industrial clients, we have newly established an ***Industrial Associates Group,*** mainly composed by members of the Commission on Glass of the Brazilian Ceramic Society (ABCeram) that one may find at http://abceram.org.br/membros-da-comissao/. Overall, CeRTEV's industrial funding base, initially dominated by the glass armor and bioglass industrial sector, has greatly diversified meanwhile, now also including major contributions from companies interested in the optical and electrical properties of glasses and glass-ceramics.

[12] Resumir os resultados de transferência de conhecimento (incluindo, mas não limitado a tecnologia, patentes, software, bases de dados, produtos, políticas públicas e outros). Deve-se também indicar o link para a página de resultados de Propriedade Intelectual do Centro, conforme o email enviado aos Cepids em 26/10/2016).

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 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 bio applications, exploiting the two CeRTEV patents BR 10 2013 020961 9 and BR 10 2014 003817 5, which have meanwhile also been filed (and granted) in the United States and Europe. They concern the development and wide application potential of the bactericidal glass F18, described in the Research Highlights Section. Our spin-off company is now also supported by two recently approved I**nnovative Research in Small Business** (PIPE/ FAPESP) grants, entitled *Development of Methodologies for the Production of High Purity Bioactive Glasses in Industrial Scale* and *Development of green-friendly cosmetics with bactericidal and healing effects for anti-acne application*, both supervised at UFSCar by E.D. Zanotto and Oscar Peitl.

Regarding the area of ***innovation and technology transfer promotion*** CeRTEV takes pride in its extensive patent application record, with currently 12 patents in the area of glass synthesis and processing under examination by the INPI (expected review period 7-10 years) and one extended abroad. For patent details, please refer to the regular annual reports, which also summarize CeRTEV's continuing efforts in the area of technology transfer promotion through ***industrial workshops and discussion groups***. This effort has been recently supplemented by the first effective steps on installation of a ***webpage*** (in Portuguese) on glass science and technology named ***Wikividros****;* at https://wikividros.eesc.usp.br/ (under construction), to serve as an open collaboration and discussion platform with partners and clients from industry. CeRTEV's Technology Transfer agenda has recently received significant professional recognition: E.D. Zanotto was honored with the award *Pawn of Technology* from the Technological Park Foundation of São Carlos (ParqTec). Since 1993 the title is awarded by the business community to major contributors to technology innovation to increase production, quality and competitiveness of products, processes and services; see http://agencia.fapesp.br/19052; http://www.abc.org.br/article.php3?id_article=3330; http://www.abividro.org.br/noticias/edgar-dutra-zanotto-recebe-o-titulo-de-peao-da-tecnologia. Professor Zanotto was also recently appointed to serve as the Chair of the Scientific Council of the ***Instituto Serrapilheira***, the first private research foundation within Brazil. Serrapilheira is financed by the donation of R$ 350,000,000 to a patrimonial fund, made by documentarist João Moreira Salles, from the founding family of Unibanco, and his wife, Branca Moreira Salles. Its annual budget of R$ 18,000,000 will be allocated exclusively towards funding bold, ground-breaking, and truly outstanding work in science and technology. While this initiative cannot alleviate the currently dramatic erosion of federal and state resources available for scientific activities in Brazil, its focus on first-rate and cutting-edge research does address an important gap in the current national research funding scenario. In our view, the selection of CeRTEV's director for this particular assignment is vivid testimony of our CEPID's documented success in the areas of basic science and technology.

Link to the RIDC Intellectual Property webpage: http:// http://www.certev.ufscar.br/innovation-1

4. Education and Dissemination Report (max. 2 pages)

The CeRTEV Education and Outreach strategy encompasses two general ***Groups of Action***: ***Group A*** aims at developing and bolstering professional qualifications in glass science and technology, while ***Group B*** strives to promote glasses as strategic materials to both targeted audiences and the general public.

An important highlight in ***Group A*** has been the development of a Technical Course on Glass Science to educate trained professionals for the glass industry, as presently there is no vocational training in this field. Together with our partners ABIVIDRO, (Brazilian Association of Automated Glass Industry) and the Paula Souza Center, a São Paulo State Government office which now administers 214 Technical Schools (ETECS) and 59 Faculties of Technology (FATECS) in 163 municipalities), we have developed a full curriculum for a three-semester course. The course includes 450 hrs of theoretical training in glass formulation, physical processes, energy management, workplace and environmental safety, and entrepeneurship and 850 hrs of practical operations. Students may start this specialization in parallel to the second year of high school or at any time if they have completed the high school. The course will be held in the city of Mogi das Cruzes (70 km distant from the city of Sao Paulo), which is the site of an important Brazilian glass industry, ***Nadir Figueiredo***, which holds one of the Technical Schools from Paula Souza Center. The laboratory infrastructure of this Technical School will accommodate the course, following necessary renovations, which will be funded by Nadir Figueiredo. 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.

The second highlight in this area has been the ***Sao Paulo Advanced School on Glasses and Glass-Ceramics,*** a 9-day workshop held at USP in August 2015. Approximately 100 highly qualified doctoral and Master students from 19 countries (35 Brazilian attendees) participated. The school covered state-of-the art topics on glass and glass ceramics, including thermodynamics, crystallization, structure/property relations and informatics, delivered in 11 2-hour lectures and three tutorials. In addition, within groups of typically 4-5 participants, the students were guided by CeRTEV faculty to develop proposals for innovative research projects, which were presented on the final day of the workshop. Based on the highly positive evaluation feedback, we are confident that the attendees have benefitted greatly from this School and returned home to their workplaces 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 them and their advisors.

Aside from these highlights, CeRTEV members do their part in developing and presenting ***workshops*** in glass science and characterization 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 of our 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

Activities developed in ***Group B*** include many highlights, detailed in the regular annual reports. CeRTEV has mounted an extensive ***ACIEPE effort*** (activities for the integration of education, research and extension) spearheaded by the UFSCar´s Rectorate. In this activity, undergraduate students from UFSCar,

under the supervision of a CeRTEV member, have access to a public elementary school, in which they discuss suitable science topics. In a second step, those elementary school students, aged 9-12 years, visit the Laboratory of Vitreous Materials, LaMaV/DEMa/UFSCar, one of the main CeRTEV laboratories. During the past two years we were able to reach out to approximately 400 students in this way. In addition, our collaboration with the ***Ouroboros Group for the Dissemination of Science*** has helped us to reach out to hundreds of students with presentations of timely scientific 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 pieces 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 compose 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/ and http://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 provided the background for 18 newly created 1-minute ***radio presentations*** on the topic of glass ***(Vitreous Minute)*** broadcasted via Radio UFSCar 95.3FM.

Further highlights of CeRTEV's outreach effort include the development of informative and creative ***printed Materials*** and ***websites***. In a two month campaign, 3 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. Volume 1 deals with basic properties and the history of glass; Volume 2 is about glass production and recycling. Volumes 3 and 4 introduce optical fibers and bioglasses. A fifth volume, entitled'The Glass Age" is still being created. These Comics Books may be seen at: http://www.vidro.ufscar.br/#manga

It goes without saying that CeRTEV maintains a regular presence at the major ***science fairs*** (e.g. SBPC, SNCT, Circus of Science, etc.) held in the State of São Paulo; having organized and/or participated in about a dozen of such events during the past three years. In this connection we wish to highlight the itinerant ***Exhibition "Glass World"*** developed by us, which features experimental demonstrations of properties and curiosities associated with vitreous materials, including light transmission by optical fiber, 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 events, reaching out to a total audience of about 30.000 attendees.

In summary, together with our partners we have developed a strong professional qualification strategy and a creative and highly diversified science dissemination program with focus on glasses. Both our ***Groups of Action*** have already generated a tremendous amount of interest and positive feedback. Thus, we feel that

CeRTEV's educational effort is making a substantial contribution to ensure a sustained growth of the glass and glass ceramic technology sector within the State of São Paulo and in Brazil on the whole.

5. List of additional funding sources, except FAPESP[13]

Please, in the first column indicate the sources of funding. In the others columns, the actual expenditure (Brazilian Reais R$) by the RIDC in the period **August 2015 – July 2017**.

Source of resources, except FAPESP	Equipment costs (capital)	Other direct costs (custeio)	Professor Salaries	Staff Salaries	Scholarships
CAPES					1.353.116
CNPq		400.473			525.681
Professors CNPq bolsas					205.532
Others					1.097.242
International projects		1.850.639			
Companies (end (after 06/2015)		887.477			
UNESP			295.253,14		
UFSCar			2.841.272,14	203.225	
USP		47.960	3.219.849,10	997.568	
Total		**3.186.549**	**6.356.374**	**1.200.793**	**3.181.571**

Overall total ~ R$ 14 million

6. Evaluation of Institutional Support[14]**:**

The CeRTEV has 6 faculty from UFSCar, 7 from USP, São Carlos campus, and 1 from UNESP - Araraquara campus.

Institutional commitment by UFSCar

The institutional support offered by UFSCar to our center has been quite substantial and helpful. A young faculty (Dr. Marcello R. B. Andreeta) was hired by the Department of Materials Engineering - DEMa in 2014 - and immediately joined the CeRTEV team. A manager, "gestora", with a degree in administration

[13] Lista de financiamentos obtidos pelo Centro de fontes outras, excluindo a FAPESP. Deve-se incluir salários de docentes e servidores diretamente ligados ao Centro, como técnicos e apoio administrativo, e demais despesas custeadas pelas respectivas universidades. A tabela deve ser preenchida com o montante total recebido no período. Exemplos: 1) somar todas as bolsas e período total: uma bolsa PD - CNPq, doze meses (valor da bolsa X 12) + cinco bolsas PD – CAPES, 24 meses (5X valor da bolsa X 24); 2) somar os montante efetivamente gastos de recursos de outras agências como edital Universal CNPq + montante efetivamente gasto de recursos FINEP + INCT, etc); 3) somar os salários dos pesquisadores principais e associados dedicados ao CEPID no período de dois anos cobertos pelo relatório; 4) somar os salários dos funcionários técnicos e administrativos dedicados ao CEPID no período de dois anos cobertos pelo relatório. Apoios efetivamente gastos em moeda estrangeira deverão usar a cotação de R$ 3,2 para conversão do dólar.

[14] Além dos valores financeiros/econômicos indicados no quadro acima, incluir informações que julgar pertinentes envolvendo a contrapartida institucional. Eventuais dificuldades também devem ser aqui reportadas.

(Ms. Laurie Leonardo) was also hired and works at the Vitreous Materials Lab of DEMa (CeRTEV´s headquarters). She has been of tremendous help with all the administration of 14 faculty and about 60 students of the center.

Additionally, an intern in computer science (Mr. Henrique Guarnieri), was also hired and spends 12 hours per week at LaMaV giving support to all computer maintenance and construction of the webpage (www.certev.ufscar.br)

Finally the UFSCar research administration office (with 3 administrative personnel) has also been of great help with all the complex materials purchasing bureaucracy and especially importation of materials and equipment of the CeRTEV team and the annual accounting paperwork.

UFSCar´s audio and TV facilities are being used to produce a series of education and outreach videos. You will find them at YouTube with the keywords "lamav", or "certev" or "edgar zanotto".

Institutional commitment by USP

Besides the USP institutional commitment already detailed in the CEPID first proposal, below we point the extra support which arose with respect to CeRTEV activities, guaranteeing to a large extent its activities.

Physical space

In January, 2014, the Group of Ceramics of the Department of Materials Engineering (SMM), EESC, moved from a lab of 40m^2 in the former SMM building at USP's Area 1 in São Carlos, shared with three principal investigators, to completely new facilities in the campus Area 2. The new ceramic and glass lab now has 291m^2. The new SMM totals approximately 4,500m^2, which includes the investigators' office and several common purpose laboratories (user facilities): thermal analysis, chemistry lab, machine shop, thermal treatments, mechanical property characterization, sample preparation, optical and electrical microscopy, and x-ray diffraction, among others, besides the lab space specifically dedicated to glass-ceramic research. About US$ 3,120,000.00 has been spent from University of São Paulo funds for constructing the building, establishing the facilities and purchasing equipment, materials and costs.

IFSC made 50m^2 of space available and paid for the renovation costs to house the new NMR spectrometer acquired by CeRTEV. The ESR lab had also significant improvements done when the spectrometer was moved to its current location. USP has provided funds for purchase of construction materials, electrical installation, internet connection, materials and labor for building and facilities.

Research support at IFSC and EESC-USP

The Hybrid Materials Technology Center (CTMH/USP) is an interdisciplinary and multidisciplinary partnership for research, development and innovation in hybrid materials and materials interrelationships during fabrication processes, which joins the SMM/EESC with the Group of Crystal Growth and Ceramic Materials of the Physics Institute of São Carlos (IFSC). The CTMH started its activities in 2011 with an initial budget of US$ 500,000 for a Scanning Electron Microscope with Field Emission Gun (SEM/FEG) and EDS, and US$ 17,000.00 for materials and costs, funded by USP. These facilities are already available and operating smoothly at EESC. USP is also responsible for the salary of the specialized technician responsible for operating the equipment.

Innovation support at EESC and IFSC

The USP Agency for Innovation assisted us during the *CeRTEV Meeting in the 5th Week USP on Intellectual Property and Innovation*. It also gave us support on the analysis of a research contract being formalized between the Itaipu Technological Park and EESC and with the Rhodia/EESC Project.

Institutional commitment of UNESP

The Chemistry Institute of UNESP in Araraquara has provided all the means necessary for the development of this project. Just after Prof. Marcelo Nalin's appointment and arrival in Araraquara (May 2013), the head of the Inorganic Chemistry Department and Dr. Sidney Ribeiro offered space in his laboratory to accommodate all the equipment and students. This laboratory, now shared with Prof. Ribeiro´s group, has around 200m^2 with numerous facilities. Small adaptations of the local infrastructure were necessary concerning air conditioning, electricity panel, etc. to accommodate the equipment. The institute director also assumed the responsibility and offered all the necessary furniture for Nalin´s laboratory. In the Institute they have some multi-user equipment, to which the Nalin group has unrestricted access. Therefore the support given to Nalin and his group was quite substantial.

7. Publications / citations URL[15] MyResearcherID: http://www.researcherid.com/rid/J-6817-2015

Google Scholar: https://scholar.google.com.br/citations?user=AG2Y4LsAAAAJ&hl=pt-BR

8. International Advisory Board Reports[16] http://www.certev.ufscar.br/research-1/review-reports-int.-advisory-board

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[15] URL das publicações do CEPID no *MyResearcherID* e no *Google Scholar*, conforme definido na avaliação de 2015 e reafirmado no e-mail aos Cepids de 26/10/2016. Em cada uma delas, listar todas as publicações resultantes de pesquisas realizadas pelo Centro apenas do período de vigência do CEPID, ou seja, a partir de 2013. Pode-se incluir uma lista de produção de resultados que eventualmente não constem das duas páginas, se julgar relevante.

[16] Por gentileza, anexe todos os relatórios e documentos produzidos pelo Conselho Consultivo Internacional do Cepid (*International Advisory Board*), devidamente identificados com número, data e autoria. Na página do Cepid sob sua responsabilidade, deve ser criado um espaço, acessível mediante senha, com todas essas informações.