

# FLASH SINTER-CRYSTALLIZATION: A NEW TECHNIQUE FOR ULTRAFAST CRYSTALLIZATION OF GLASSES

João Vitor Campos, Federal University of São Carlos  
Joao.campos@ufscar.br  
Isabela Reis Lavagnini, University of São Paulo  
Vinicius Martins Zallocco, Federal University of São Carlos  
Eliria Maria de Jesus Agnolon Pallone, University of São Paulo  
Eduardo Bellini Ferreira, University of São Paulo  
Ana Candida Martins Rodrigues, Federal University of São Carlos

Key Words: flash sintering, impedance spectroscopy, sintering, glass-ceramics, batteries.

In the present work, we propose *Flash Sinter-Crystallization* – a new technique to crystallize and sinter glasses compacted powder in a single step. For that, we prepared a  $\text{Li}_2\text{O} - \text{Al}_2\text{O}_3 - \text{GeO}_2 - \text{P}_2\text{O}_5$  glass by melt-quenching the stoichiometric mixing of the precursor oxides for obtaining  $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$  (LAGP), further details in [1]. The glass pieces were then milled and uniaxially pressed (250 MPa) as pellets of 5 mm height and 6 mm diameter. The pellets samples were flash sinter-crystallized at a constant heating rate of  $20\text{ }^\circ\text{C}/\text{min}$  at a maximum furnace temperature of  $500\text{ }^\circ\text{C}$  applying an electric field of  $150\text{ V}\cdot\text{cm}^{-1}$  and a preset maximum current density of  $10 - 100\text{ mA}\cdot\text{mm}^{-2}$  (ten conditions equally spaced). We controlled the power surge as a ramp to avoid a power peak during the flash event. We varied the holding time of the flash state from 20 s to 2 h. Differential scanning calorimetry was used to measure the parent glass transition ( $522\text{ }^\circ\text{C}$ ) and crystallization peak ( $622\text{ }^\circ\text{C}$ ). X-ray diffraction was used to assess the phases and crystallinity. Electrochemical impedance spectroscopy under temperatures of  $30\text{ }^\circ\text{C} - 170\text{ }^\circ\text{C}$  was used to measure the ionic conductivity and activation energy of the flash sinter-crystallized specimens. The flash transition happened at  $468 \pm 7\text{ }^\circ\text{C}$  for all conditions (below glass transition). After flash sinter-crystallization, the samples exhibited pure NASICON structure. In general, the samples' crystallinity, crystallite size, and ionic conductivity increased with the preset maximum current density and holding time. The best results were achieved when a condition of  $50\text{ mA}\cdot\text{mm}^{-2}$  and 30 min holding time was used. In this case, the ionic conductivity of the flash sinter-crystallized sample surpassed the one conventionally crystallized for 12 h at  $850\text{ }^\circ\text{C}$  ( $0.21\text{ mS}\cdot\text{cm}^{-1}$  and  $0.12\text{ mS}\cdot\text{cm}^{-1}$ , respectively). We concluded that the rapid heating promoted by the flash event and a possible athermal effect related to the electric field allowed rapid crystallization of the glass and resulted in a NASICON structure electrolyte with conductivity comparable with others conventionally sintered for several hours.

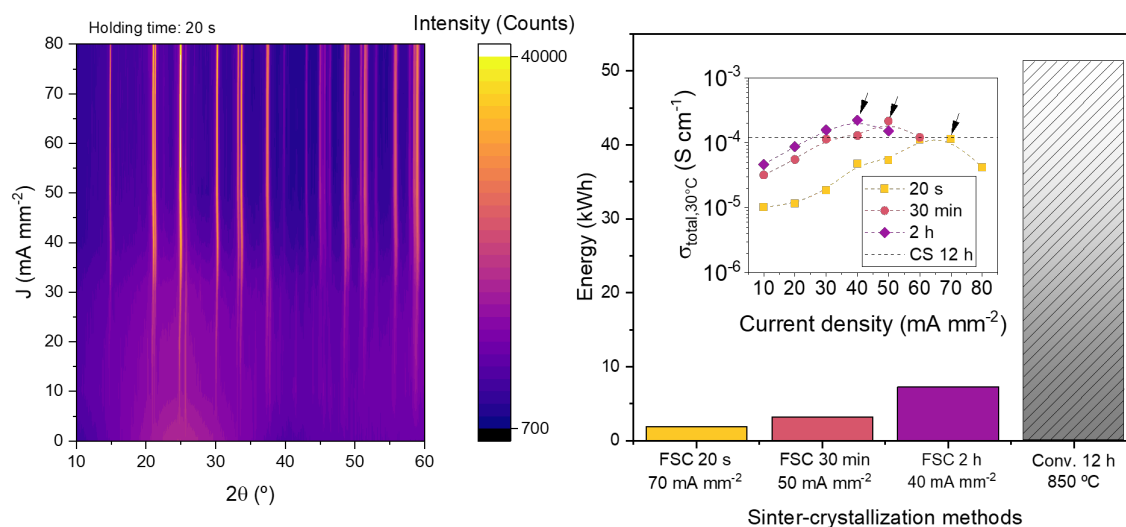


Figure 1 Color map plot of the XRD results of LAGP flash sinter-crystallized samples under different current densities (y-axis) and 20 s holding time (left); Energy consumption of each sinter-crystallization process (right) and the samples' total ionic conductivity at room temperature for the different experimental conditions (inset).

## References

[1] C. Schröder; J. Ren; A. C. M. Rodrigues; H. Eckert, J. Phys. Chem. C, 118, 2014, 9400-9411.