Dielectric and Catalytic Behavior of V_2O_5-Rich Glass-Ceramics Synthesized by Controlled Heat-Treatment-Induced Crystallization

Sara Marijan[1,*], Marija Mirosavljević[1], Teodoro Klaser[1], Petr Mošner[2], Ladislav Koudelka[2], Željko Skoko[3], Jana Pisk[4], Luka Pavić[1]

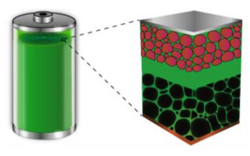
[1] Division of Materials Chemistry, Ruđer Bošković Institute, Bijenička cesta 54, Zagreb, Croatia
[2] Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, Pardubice, Czech Republic
[3] Department of Physics, Faculty of Science, University of Zagreb, Bijenička cesta 32, Zagreb, Croatia
[4] Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, Zagreb, Croatia

*smarijan@irb.hr

MDPI applied sciences

THE GLOBAL CHALLENGE

- development of novel, more sustainable, efficient, and environmentally friendly materials for electrochemical devices and catalysts



SOLID-STATE BATTERIES
- high voltage
- extended cycle-life
- reduced safety risks

RENEWABLE DIESEL FUEL
- reduces greenhouse gas emissions
- lower-toxicity

WHY V_2O_5-BASED MATERIALS?

- promising cathode materials for Li-ion, Na-ion, and all-solid-state batteries
  - high safety, energy density, and long life cycles
- promising catalysts in oxidation reactions
  - fatty acid decarboxylation
    - crucial for renewable biodiesel production → lower-toxicity alternative to petroleum diesel

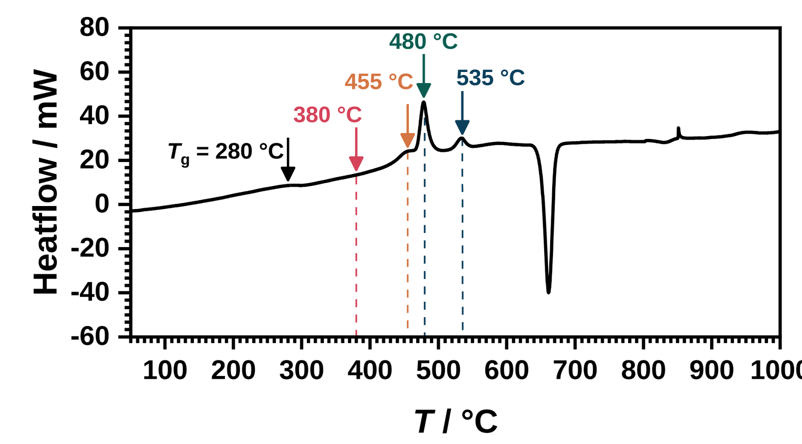
WHY GLASSES AND GLASS-CERAMICS?

- great compositional flexibility
- easy glass preparation process at low temperatures
  - melt quenching technique
- easy glass-ceramic preparation process
  - controlled heat-treatment-induced crystallization of parent glass → unique control over composition, crystallographic structure, and microstructure

PREPARATION OF GLASS & GLASS-CERAMICS

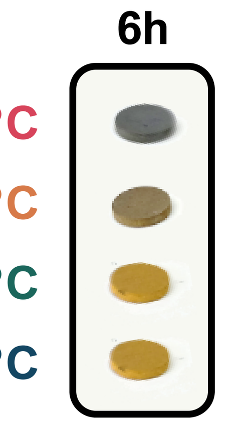
1. Glass synthesis
   - Homogenization of starting mixture
   - Melting & Casting

$70V_2O_5$-$20Nb_2O_5$-$10P_2O_5$ glass (AS IS)
- black opaque glass



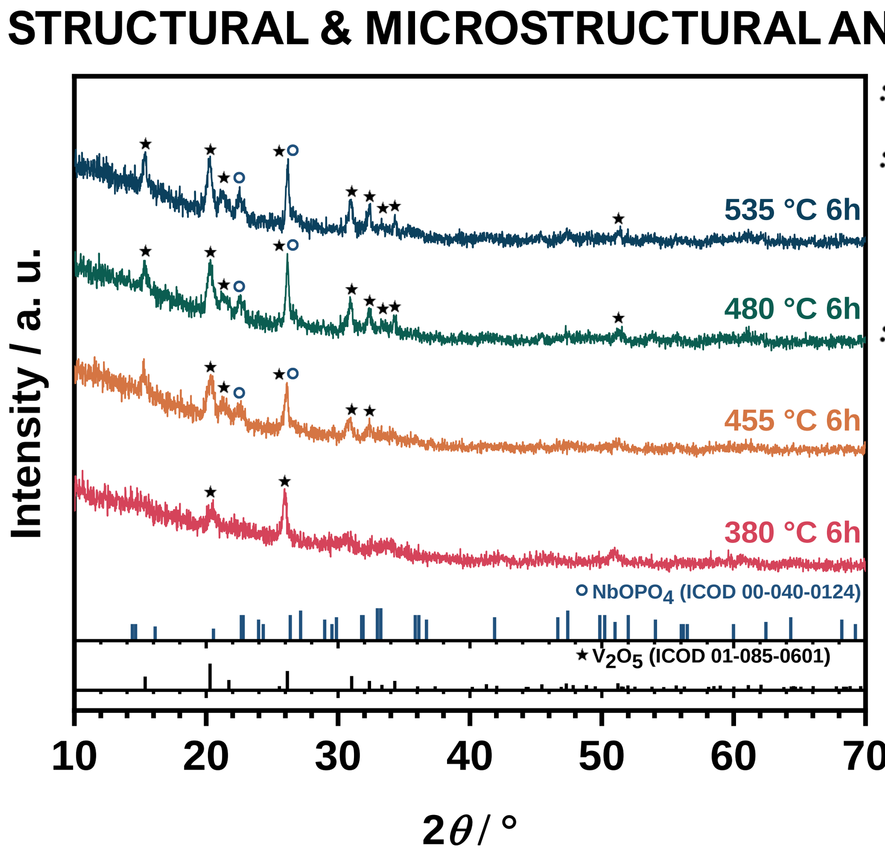
DTA curve of $70V_2O_5$-$20Nb_2O_5$-$10P_2O_5$ glass (AS IS)

2. Glass-ceramic (GC) synthesis
   - Crushing glass into powder
   - Pressing in order to form a pastille
   - Controlled crystallization



GC samples

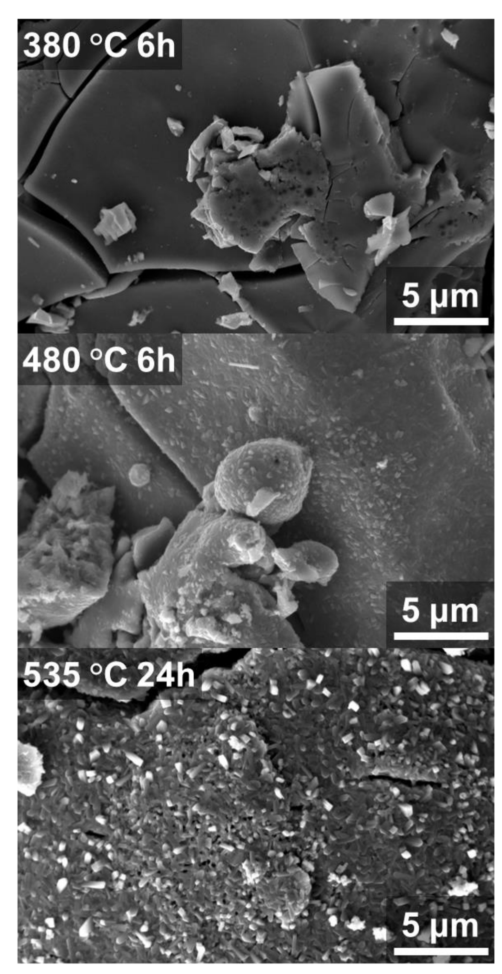
STRUCTURAL & MICROSTRUCTURAL ANALYSIS



PXRD patterns of GCs prepared by heat treatment of $70V_2O_5$-$20Nb_2O_5$-$10P_2O_5$ glass at varying temperatures for 6h.

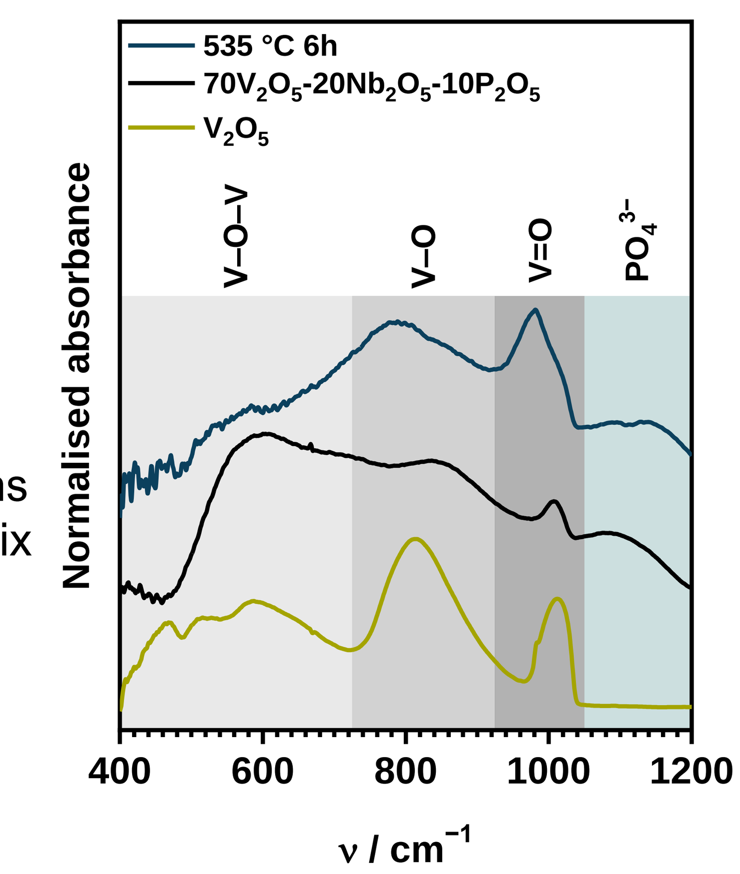
- 380 °C: V_2O_5
- 455 °C/480 °C/535 °C: two crystalline phases, V_2O_5 & $NbOPO_4$
- Rietveld analysis: crystallization temperature ↑ crystalline phases ↑
  - V_2O_5: 18–43%
  - $NbOPO_4$: 19–24%

  amorphous phase ↓
  - 82–33%



SEM micrographs of prepared GCs.

- 380 °C: dominantly amorphous glass matrix
- 455 °C/480 °C: partially crystallized; elongated nanorod grains embedded in glass matrix
- 535 °C → dominantly crystallized; aggregated elongated grains (nano- to micrometer scale)

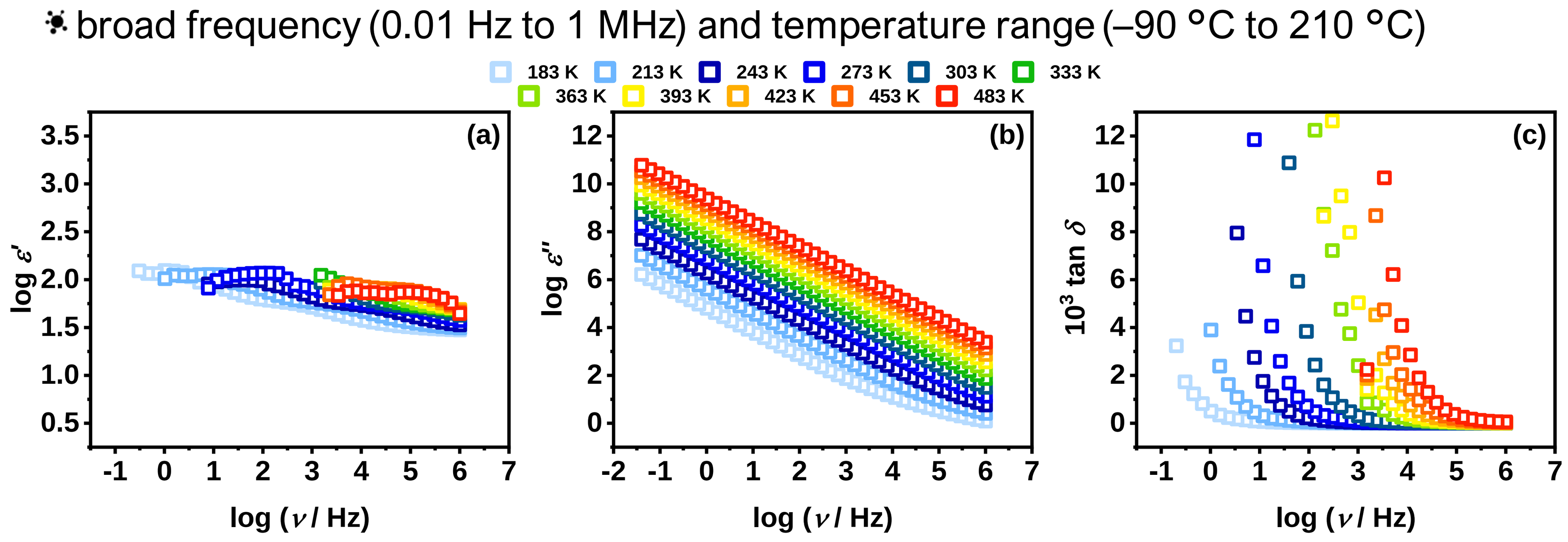


IR spectra: 535 °C 6 h GC, $70V_2O_5$-$20Nb_2O_5$-$10P_2O_5$ glass and commercial V_2O_5.

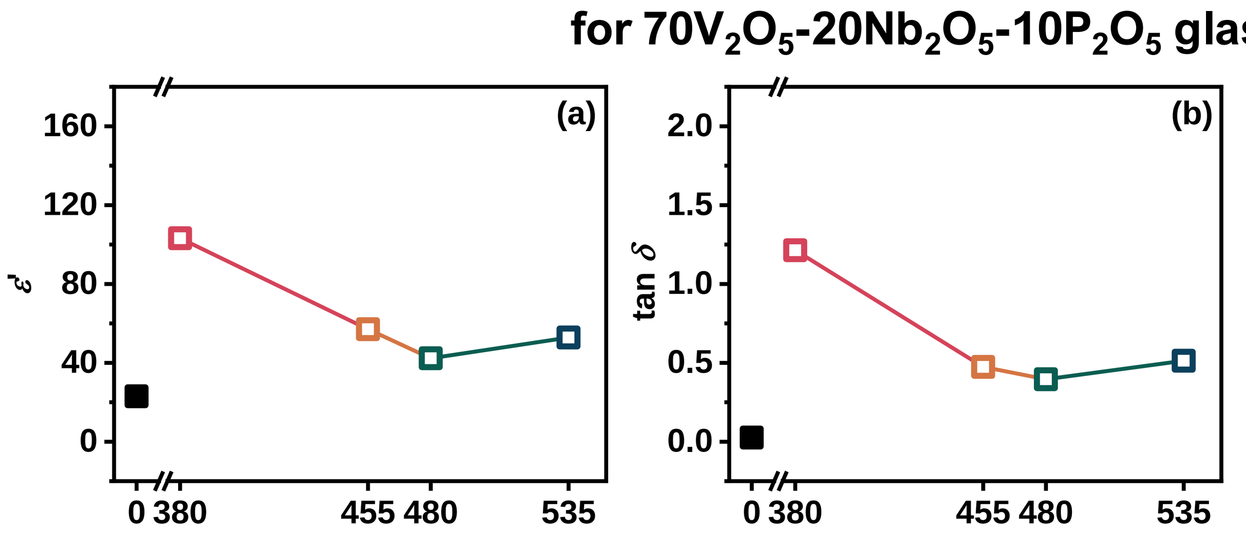
- GCs vs glass → similar IR spectra
- no significant changes in the appearance of GCs spectra with varying temperatures of controlled crystallization
- GCs predominantly consist of the V_2O_5 crystalline phase → similar spectral features: VO_x units interconnected through V–O–V bonds

DIELECTRIC PROPERTIES

- impedance spectroscopy (IS)
- broad frequency (0.01 Hz to 1 MHz) and temperature range (–90 °C to 210 °C)



Frequency dependence of the (a) real, $\varepsilon'(\omega)$, and (b) imaginary, $\varepsilon''(\omega)$, parts of the complex permittivity and (c) loss factor, tan δ, at different temperatures for $70V_2O_5$-$20Nb_2O_5$-$10P_2O_5$ glass.



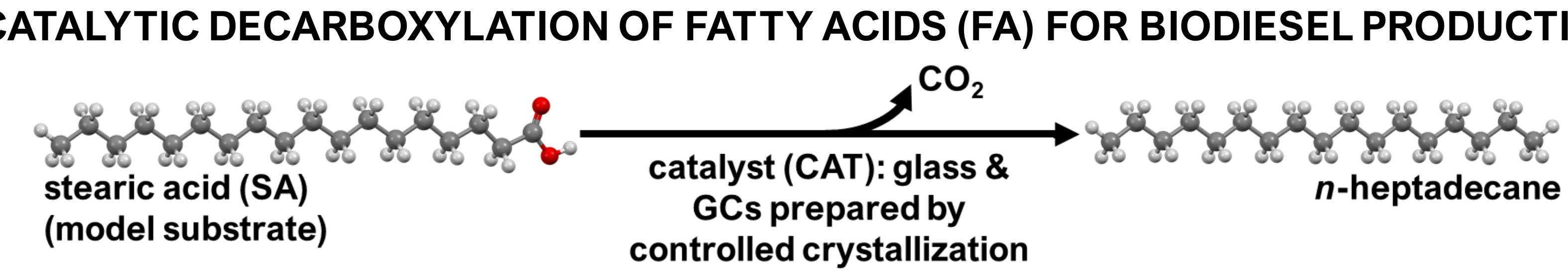
(a) Dielectric permittivity, ε_∞, and (b) loss factor, tan δ, at T = 183 K and ν = 1 MHz for $70V_2O_5$-$20Nb_2O_5$-$10P_2O_5$ glass and prepared GCs.

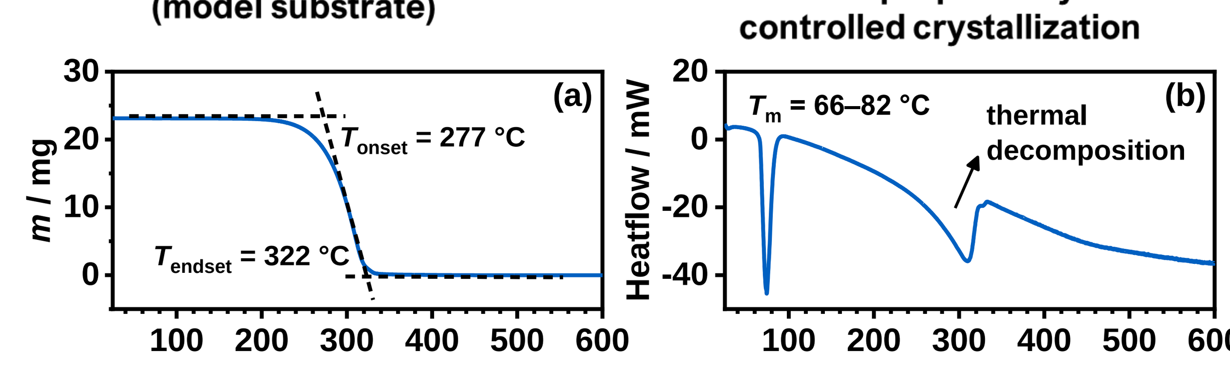
- GCs achieve higher ε' and tan δ values compared to parent glass
- 380 °C: the highest ε' and tan δ values
- 455 °C/480 °C/535 °C: ε' and tan δ values decrease with increasing crystallization temperature

CATALYTIC ACTIVITY

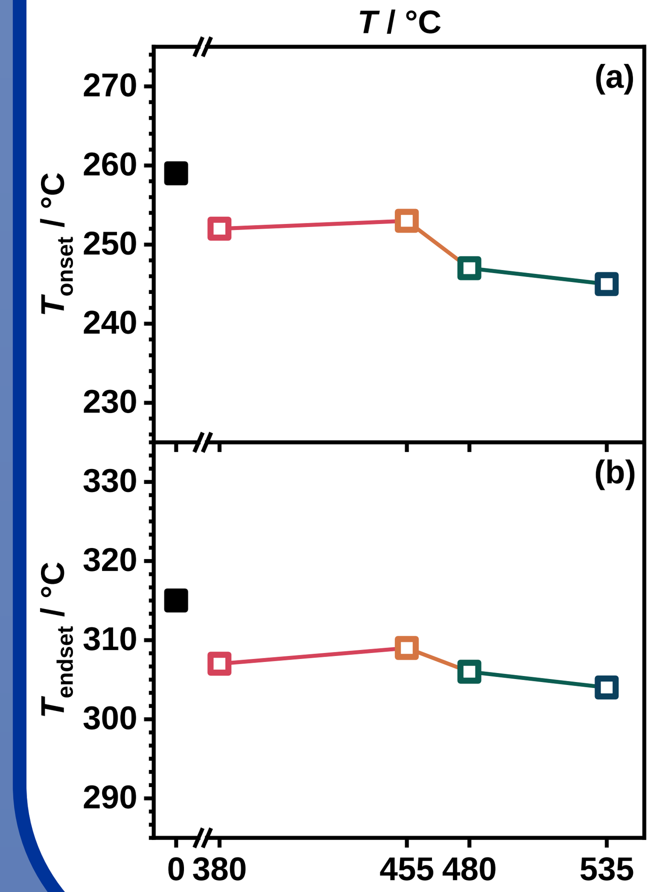
- thermogravimetric analysis and differential scanning calorimetry (TG/DSC)

CATALYTIC DECARBOXYLATION OF FATTY ACIDS (FA) FOR BIODIESEL PRODUCTION





(a) TG and (b) DSC curves of the thermal decomposition of stearic acid (SA).



Effect of catalyst (CAT) addition on the (a) onset, T_{onset}, and (b) endset, T_{endset}, temperatures of the thermal decomposition of stearic acid (SA).

- CAT: $70V_2O_5$-$20Nb_2O_5$-$10P_2O_5$ glass & prepared GCs
  - SA decomposition shifted to lower temperatures
- T_{onset} → 245–253 °C; T_{endset} → 304–309 °C
  - lower compared to pure SA (277 °C; 322 °C)
- GCs show enhanced catalytic activity compared to the parent $70V_2O_5$-$20Nb_2O_5$-$10P_2O_5$ glass
- catalytic activity increases for GCs prepared at higher crystallization temperatures
- 535 °C GC → shows the best catalytic activity

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