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Exploring the Influence of V_2O_5 Content on the Mechanism of Electrical Transport in the Na_2O-V_2O_5-Nb_2O_5-P_2O_5 Glass System: A Perspective through Model-Free Scaling Procedures

*Sara Marijan[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, 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, Zagreb, Croatia
[4]Department of Chemistry, Faculty of Science, University of Zagreb, Zagreb, Croatia

e-mail: lpavic@irb.hr

MOTIVATION

- Na-V-P-based materials are promising materials for application as Na intercalation cathodes for high-rate sodium-ion batteries
- presence of both alkali and transition metal ions, which can exist in various oxidation states (V^{4+}, V^{5+}), represents the possibility of mixed ionic-polaronic conduction mechanism which has proven to be particularly effective in cathode materials
- thermal stability can be significantly enhanced by incorporating metal oxides such as Nb_2O_5

RESEARCH AIM

- to study the influence of V_2O_5 content on the mechanism of electrical transport in two glass series:
  (A) $35Na_2O$-$10V_2O_5$-$(55–x)P_2O_5$-xNb_2O_5, x = 0–35 mol%
  (B) $35Na_2O$-$25V_2O_5$-$(45–x)P_2O_5$-xNb_2O_5, x = 0–25 mol%

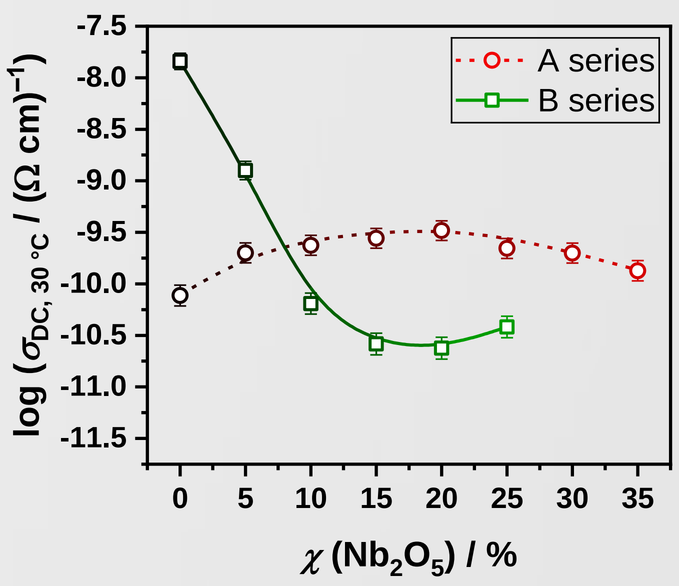
METHOD

- solid-state impedance spectroscopy (SS-IS):
  frequency range: 0.01 Hz to 1 MHz
  temperature range: –90 ˚C to 240 ˚C

DC CONDUCTIVITY

(A) series vs (B) series

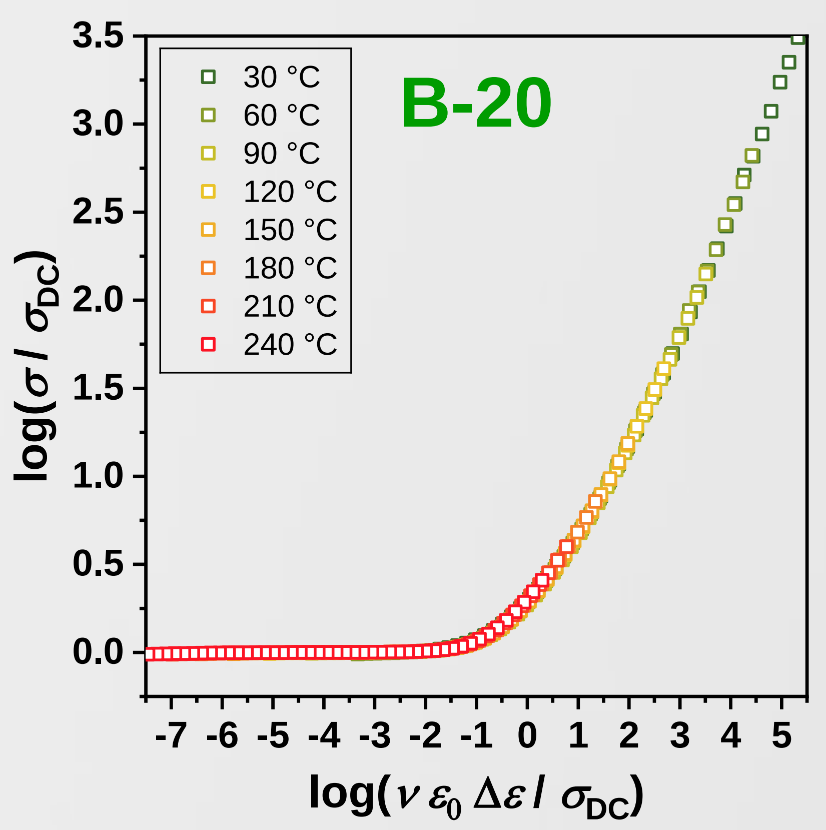
- substitution of P_2O_5 by Nb_2O_5 results in an increase in conductivity in series **(A)**, while it negatively affects conductivity in series **(B)**



Compositional dependence of DC conductivity, σ_{DC}, at 30 °C

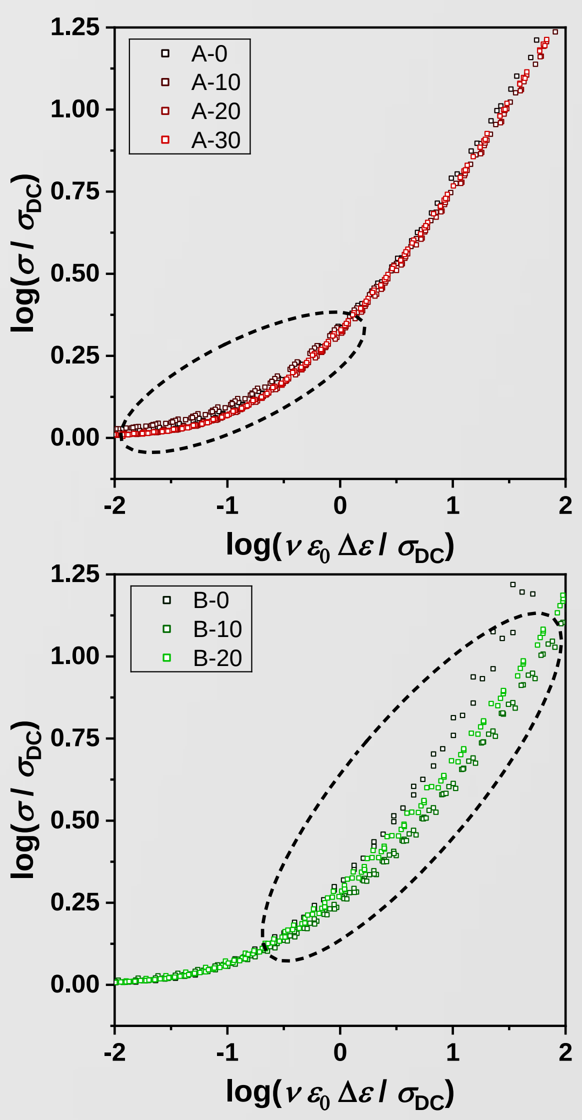
SIDEBOTTOM SCALING

- universal scaling → scaling parameters: the DC conductivity, σ_{DC}, temperature, T, and the dielectric strength of relaxation, $\Delta\varepsilon$; $(\sigma'(\nu, T)/\sigma_{DC}(T)) = F(\varepsilon_0\Delta\varepsilon\nu/\sigma_{DC}(T))$



Sidebottom scaling of conductivity spectra of B-20 glass

- master curves are obtained for all glasses from both **(A)** and **(B)** series
- **NO** super master curves due to differently shaped master curves

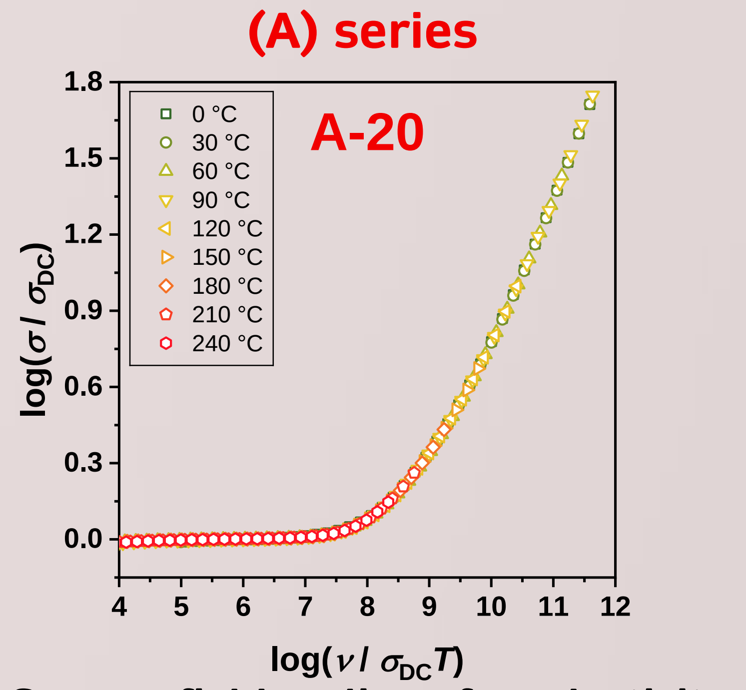


Construction of super master-curves for (A) and (B) series

SUMMERFIELD SCALING

- mobility scaling → scaling parameters: the DC conductivity, σ_{DC}, and temperature, T; $(\sigma'(\nu, T)/\sigma_{DC}(T)) = F(\nu/\sigma_{DC}(T)T)$

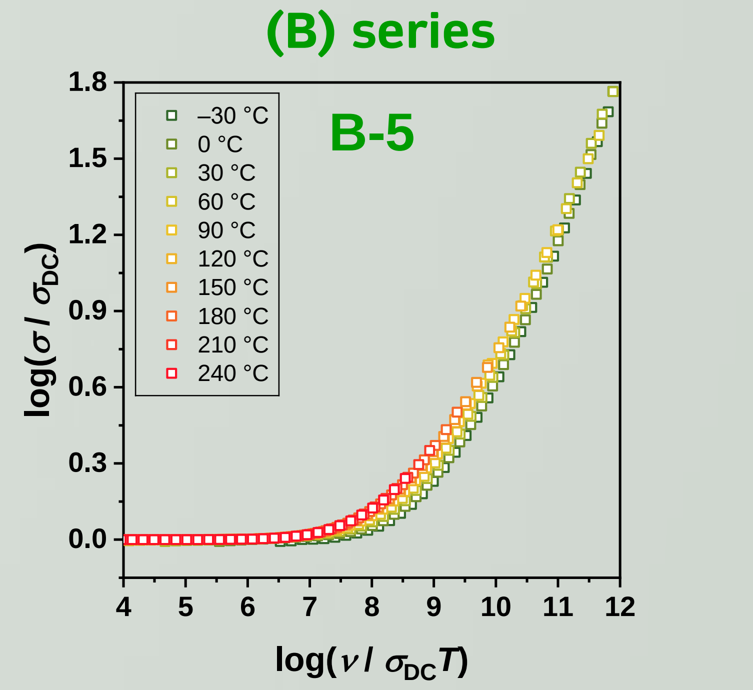
(A) series



Summerfield scaling of conductivity spectra of A-20 glass

- master curves are obtained for all glasses ✔
- transport is due to one type of charge carrier → ionic mechanism

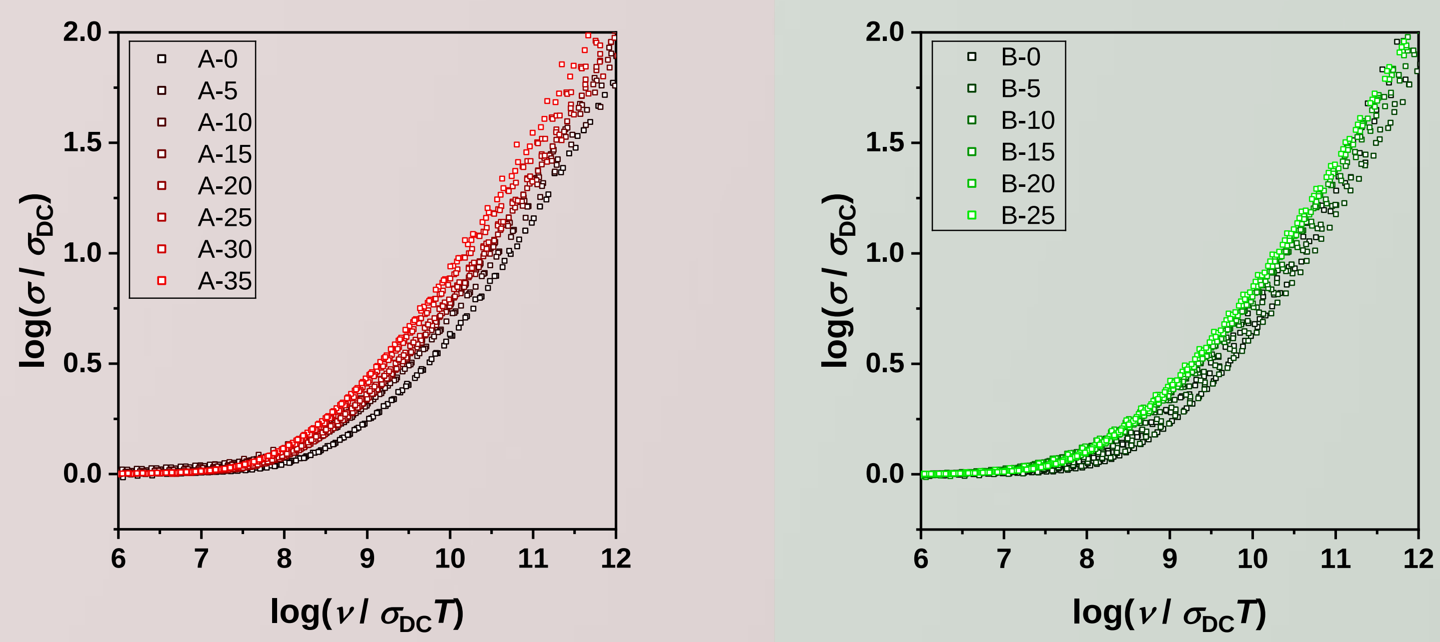
(B) series



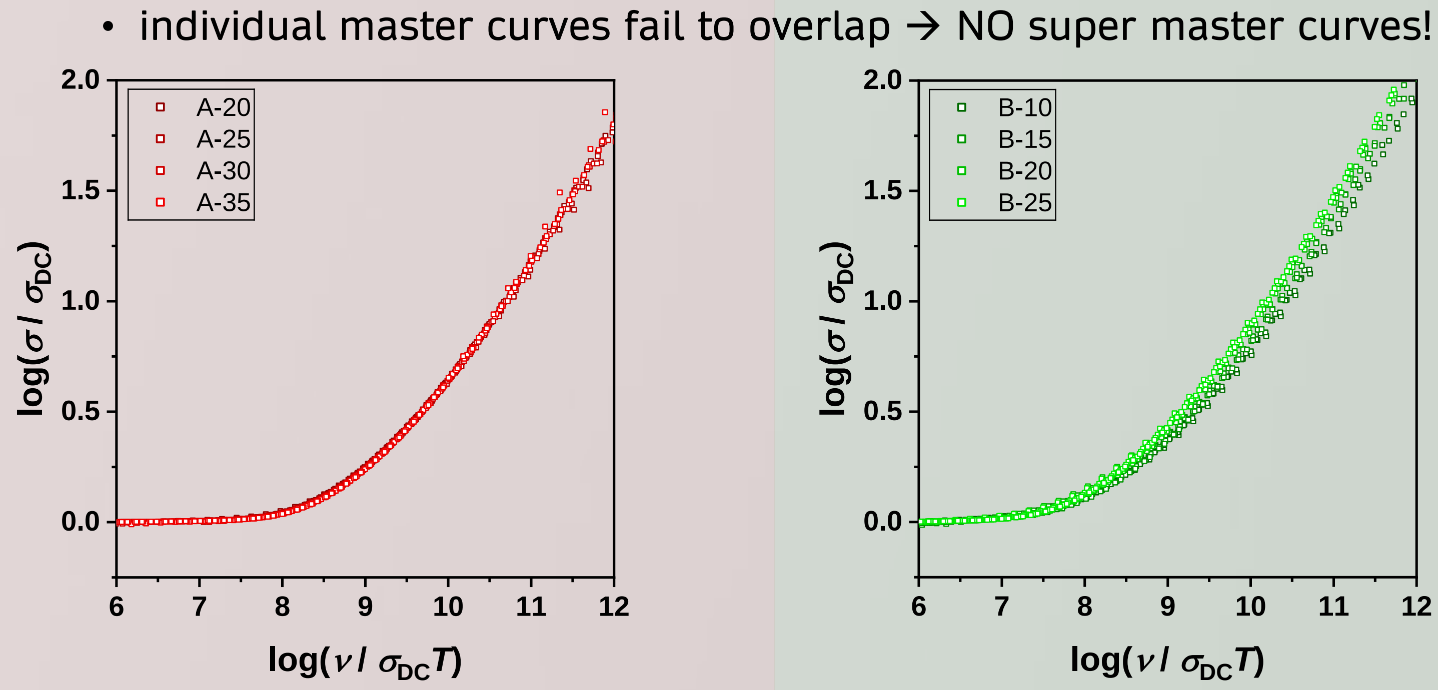
Summerfield scaling of conductivity spectra of B-5 glass

- master curves are NOT obtained for **B-0** and **B-5** glasses ✘
- mechanism changes with temperature → 2 types of charge carriers

Construction of super master-curves for (A) and (B) series



- individual master curves fail to overlap → NO super master curves! ✘



- shift along the scaled frequency axis yields super master-curve for glasses with 20 ≤ x ≤ 35 ✔
- shift along the scaled frequency axis → NO super master-curve due to differently shaped master curves ✘

CONCLUSIONS

- dual role of V_2O_5: in **(A) series** it doesn't participate in the conduction process, whereas in **(B) series** it contributes to conductivity via polaronic mechanism
- possibility of fine-tuning the mechanism of electrical conductivity via simple changes in composition