

Effect of copper content and remelting conditions on the physical properties of lithium phosphate glasses

Karolína Pradeniaková^{a)}, Francisco Muñoz^{b)}

^{a)} Department of Physics, Faculty of Electrical Engineering and Information Technology, University of Zilina, pradeniakova@stud.uniza.sk

^{b)} Institute of Ceramics and Glass (CSIC), Madrid, Spain, fmunoz@icv.csic.es

INTRODUCTION

Phosphate glasses are valued for their low melting temperatures, high thermal expansion, and good solubility of transition metal ions. Incorporating copper ions ($\text{Cu}^+/\text{Cu}^{2+}$) into their matrices influences thermal stability, colour, density, and electrical behaviour due to their variable oxidation states and potential for polaronic conduction. Our research investigates how varying copper content and subsequent treatment parameters affect glass-forming ability, thermal transitions, structure, and electrical conductivity.

MATERIALS & PREPARATION METHODS

Base system: $50\text{Li}_2\text{O} - x\text{CuO} - (50-x)\text{P}_2\text{O}_5$

Chemicals used: Li_2CO_3 (VWR), $\text{Cu}(\text{NO}_3)_2$ trihyd. (Sigma-Aldrich), $\text{NH}_4\text{H}_2\text{PO}_4$ (Thermo Scientific) all reagent grade 99%+

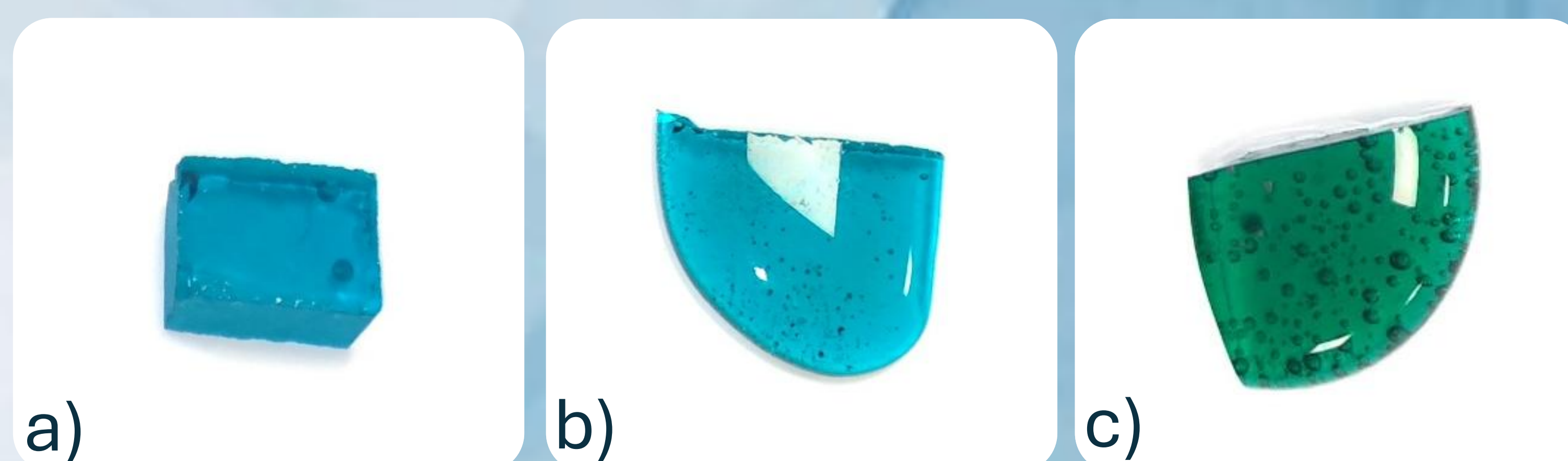
- Powdered precursors were mixed, **melted** at 800°C in a platinum crucible, then **quenched** on a pre-heated steel plate, and annealed at 325°C to remove stress
- These glasses were then cut and remelted in **nitrogen** flow at varying temperatures and time durations

CHARACTERISATION METHODS & RESULTS

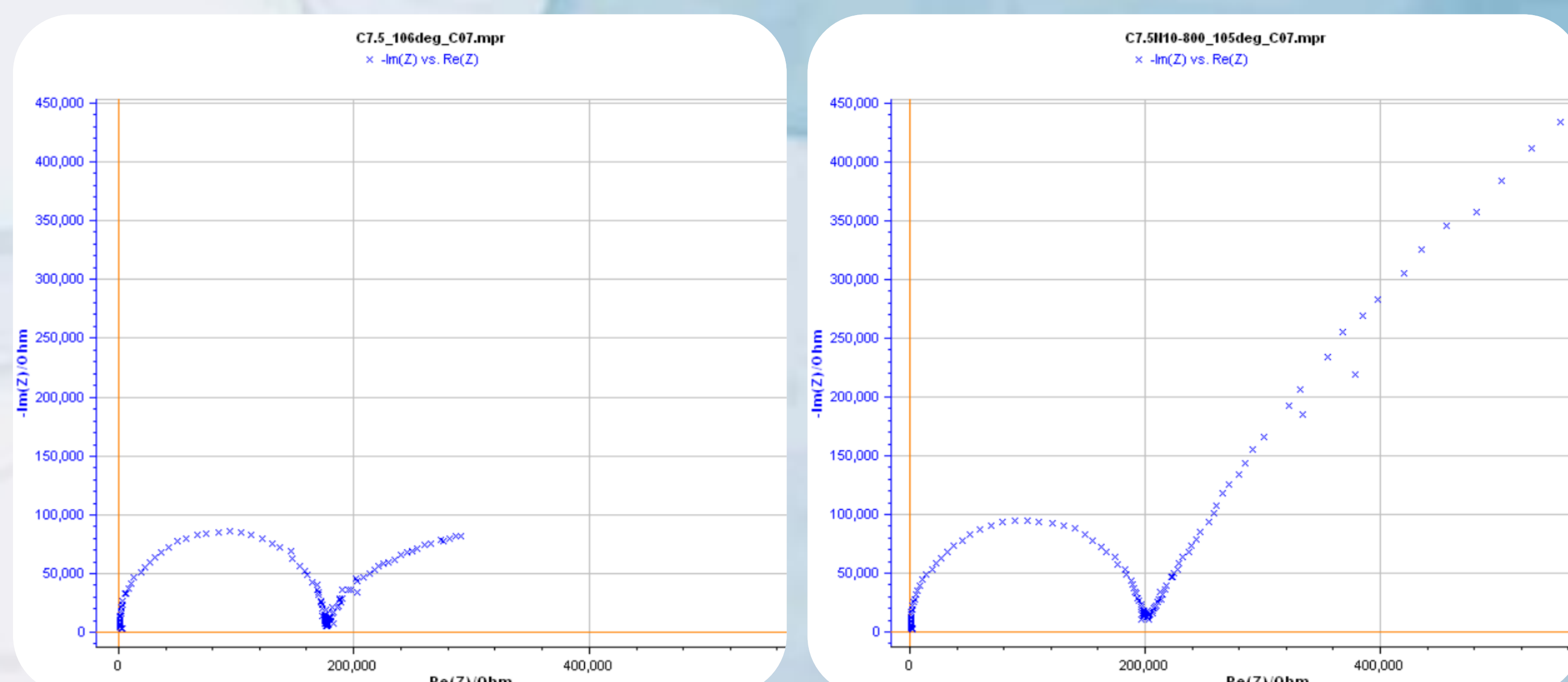
- **pXRD** (powder X-ray diffraction) confirmed glassy amorphous character of our samples together with emergence of metallic copper peaks at high treatment temperatures and/or times
- **Density** measurements using Archimedes method show a gradual decrease of density with increasing treatment temperatures and/or times, indicating some degree of depolymerization and relaxation of the glass network
- **FTIR** (infrared spectroscopy) shows a broad decrease in water-related absorption features with longer heat treatment, indicating dehydration of the samples
- **PEIS** (potentiostatic electrochemical impedance spectroscopy) was used to determine the electrochemical behaviour of our glasses. We observed a slight increase in conductivity with longer heat treatments and markedly different shapes, indicating changes in the underlying equivalent circuit behaviour
- **XRF** (X-ray fluorescence spectroscopy) and **ICP** (induction coupled plasma) were used to confirm the chemical composition of our samples, matching the calculations

CONCLUSION & PLANNED DIRECTION

Lithium phosphate glasses with varying copper concentrations were successfully synthesized and characterized using the aforementioned techniques. Nitrogen heat treatment led to notable changes in several physical and chemical properties. Future work will focus on employing additional characterization methods to gain deeper insight into the structural and functional changes induced by composition and processing conditions.



Comparison of glass samples with 5% Cu concentration, a) original glass b) treated glass at 700°C and 1 hour c) treated glass at 700°C and 10 hours – colour shift implies change of copper oxidation state with longer treatments



PEIS spectra of two 7.5% copper samples at the same temperature, one untreated (left), the other treated at 800°C for 10 hours – while both spectra show roughly the same value of resistance (intercept on $\text{Re}(Z)$ axis), the spectra show significantly different shapes

| sample ID | Cu content | remelting (nitrogen) | | activation energy | $\log \sigma$ at 25°C | density |
|-------------|------------|-------------------------------------|--------------|-------------------|-------------------------------------|---------|
| | [mol %] | temperature [$^\circ\text{C}$] | time [hr] | | | |
| C2.5 | 2.5 | 700 | | 0.79801 | -9.09700 | 2.40277 |
| C2.5N1 | | | 1 | 0.81530 | -9.04289 | 2.40552 |
| C2.5N2 | | | 2 | 0.78537 | -8.94315 | 2.40241 |
| C2.5N10 | | | 10 | 0.74817 | -8.59069 | 2.40660 |
| C2.5N2-800 | | 800 | 2 | 0.78890 | -8.82118 | 2.38861 |
| C2.5N10-800 | | | 10 | | | 2.38654 |

The table summarizes key physical and electrical properties of the glasses from one set before and after nitrogen treatment. A slight decrease in density is observed post-treatment, suggesting minor structural relaxation or network depolymerization. Electrical conductivity shows an increase, accompanied by a reduction in activation energy, indicating enhanced ion/electron mobility and changes in the conduction mechanism

ACKNOWLEDGEMENTS

We acknowledge University of Žilina (UNIZA) and Instituto de Cerámica y Vidrio (ICV – CSIC) for providing the facilities and support to conduct this research.