Investigation of $x(Fe_2O_3 \cdot Ag_2O) \cdot (100-x)[P_2O_5 \cdot CaO]$ glass samples by means of PIXE, PIGE and RBS methods

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OBJECTIVES

- Preparation of new materials with vitreous structure, based on phosphorus and calcium, doped with silver and vanadium ions
- Chemical Formula $x\left(Fe_2O_3 \cdot Ag_2O\right) \cdot \left(100 - x\right)\left[P_2O_5 \cdot CaO\right], \quad 0 \leq x \leq 0.5$
- These materials have antibacterial and antifungal properties and can be used in controlled enclosures such as swimming pools, museums, polluted waters etc.
- The confirmation of the compounds composition and stoichiometry is investigated by means the PIXE, PIGE and RBS measurements

EARLIER STUDIES

- Glasses containing transition metal ions are important materials for science, technology, and engineering, for their electrical, optical and magnetic properties that make them suitable for large number of applications in many fields.

- By the addition of transition metal oxides such as Fe_2O_3 and V_2O_5 in phosphate glasses, properties such as low glass transition temperatures, high thermal expansion coefficient, and low melting temperature are acquired by the system. The addition of iron and vanadium ions enriches the characteristics of the lithium phosphate glasses system with magnetic, semiconductor and other properties.

- Morphological, structural, spectroscopic and PIXE investigations of the system $x(Fe_2O_3 \cdot V_2O_5) \cdot (100-x)[P_2O_5 \cdot Li_2O]$ with $0 < x < 0.5$ have been accomplished.

EARLIER STUDIES

Morphological, structural, spectroscopic investigations

$x(Fe_2O_3 \cdot V_2O_5) \cdot (100-x)[P_2O_5 \cdot Li_2O]$ with $0 < x < 0.5$

- ✓ **XRD measurements** - It was obtained that the X-ray spectra of the investigated samples are characteristic of vitreous systems. No crystalline phase was observed up to 50 mol% ($Fe_2O_3 \cdot V_2O_5$).

- ✓ **Magnetic measurements** - For glasses with $x \leq 0.5$ the temperature dependence of the reciprocal magnetic susceptibility show a Curie type behavior, which shows that in this range of concentrations, the transitional magnetic ions are isolated and/or participating in the dipolar interactions .
- ✓ - Analyzing the molar Curie constant, we conclude that the amount of vanadium and iron ions in the V4 +, Fe3 +, and Fe2 + states is small compared to the total transition ions; although the presence of vanadium ions in states with a lower valence, which increase the molar Curie constant, is not excluded.

- ✓ **SANS investigations** - It was obtained, that at the nano length scales, with the increase of the concentration x the microstructure features of the system are changing from particulate to fractal; morphological dimensions of the initial system have been determined.

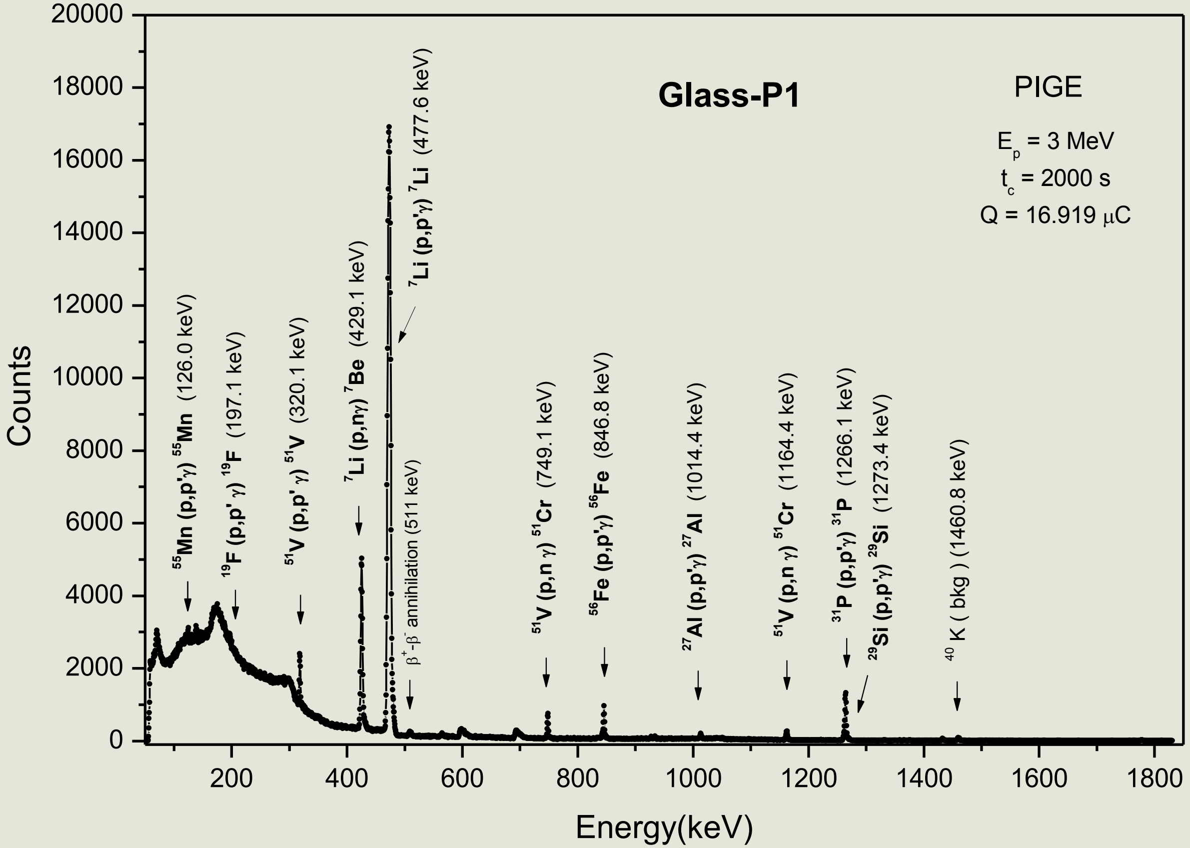
- ✓ **SEM investigations** - The structural 2D-results from SEM are in good agreement with the spatial organizations results from SANS.

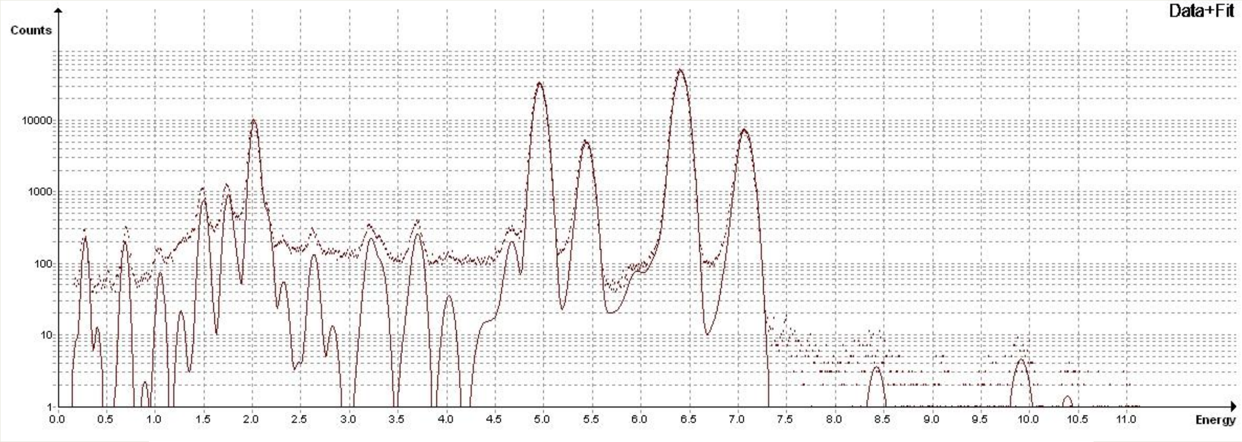
C. Andronache, M. Balasoiu, O.L. Orelovich et al., Journal of Optoelectronics and Advanced Materials, 21(11-12) (2019)

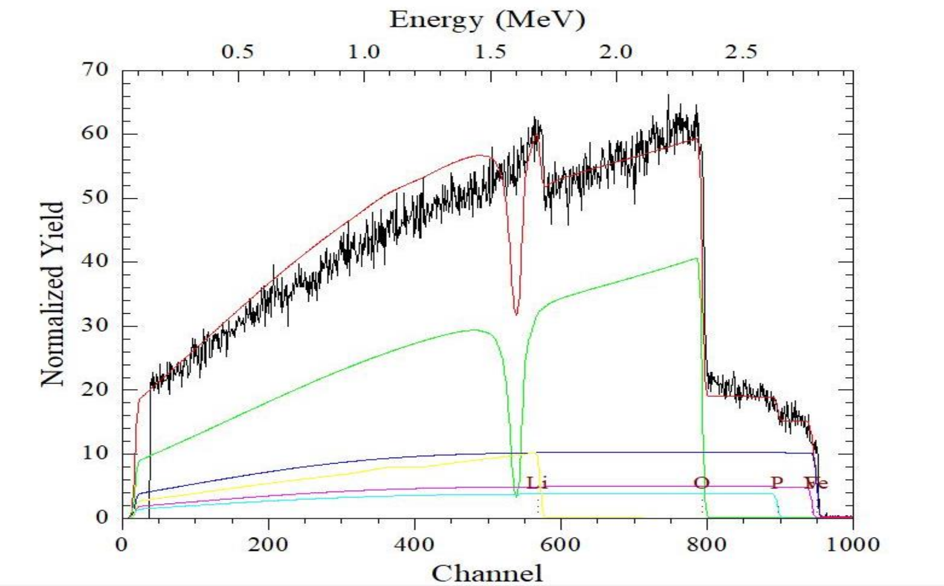
EARLIER STUDIES

PIXE, PIGE, and RBS investigations - lithium phosphate glass

$x(Fe_2O_3 \cdot V_2O_5) \cdot (100-x)[P_2O_5 \cdot Li_2O]$ with $0 < x < 0.5$







PIXE: F, Na, Mg, Al, Si, **P**, S, Cl, K, Ca, **V**, Cr, Mn, **Fe.**

PIGE **Li**, F, Na, Al, Si, **P**, **V**, Cr, Mn, **Fe**.

RBS: **Li**, O, **P**, and **Fe**.

EARLIER STUDIES

Elemental contents of lithium phosphate glass samples determined by PIGE (homogeneity study)

$x(Fe_2O_3 \cdot V_2O_5) \cdot (100-x)[P_2O_5 \cdot Li_2O]$ with $0 < x < 0.5$

Glass-P3 (x=0.2)

Elem.	Pos. 1	Pos. 2	Pos. 3	σ (%)	Average	SD (%)
Li (%)	3.51	3.58	3.73	0.5-1.5	**3.61**	3.1
P (%)	20.4	20.3	18.6	2.1-2.8	**19.8**	5.1
V (%)	6.37	6.39	6.78	8.4-14	**6.51**	3.5
Fe (%)	30.7	32.1	30.4	4.6-8.4	**31.1**	2.9

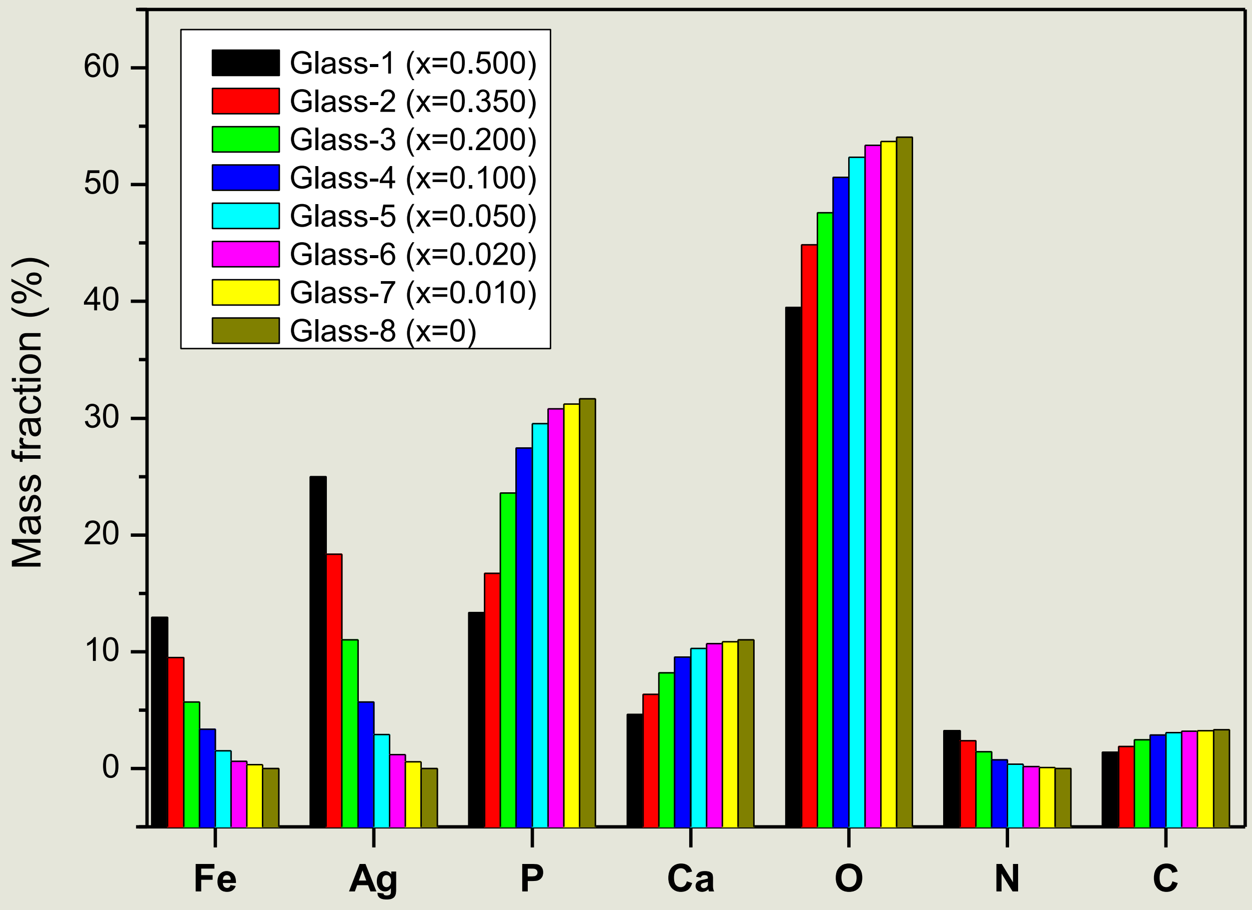
Glass-P4 (x=0.05)

Elem.	Pos. 1	Pos. 2	Pos. 3	σ (%)	Average	SD (%)
Li (%)	4.09	4.08	4.20	0.5-1.8	**4.12**	1.6
P (%)	26.2	24.2	24.9	1.6-3.4	**25.1**	4.0
V (%)	1.47	2.38	1.89	20-30	**1.91**	23.8
Fe (%)	22.7	21.9	24.3	6.2-7.7	**23.0**	5.3

Experimental

Samples preparation

$x(Fe_2O_3 \cdot Ag_2O) \cdot (100-x)[P_2O_5 \cdot CaO]$



Sample	x
1	0.5
2	0.35
3	0.2
4	0.1
5	0.05
6	0.02
7	0.01
8	0.00

For Ion Beam Analysis (IBA), the powder glass samples were prepared as **pellets** of 1 cm diameter and 1 mm thickness using a hydraulic press (4.5 t).

The pellets were secured on double carbon tape on the irradiation support.

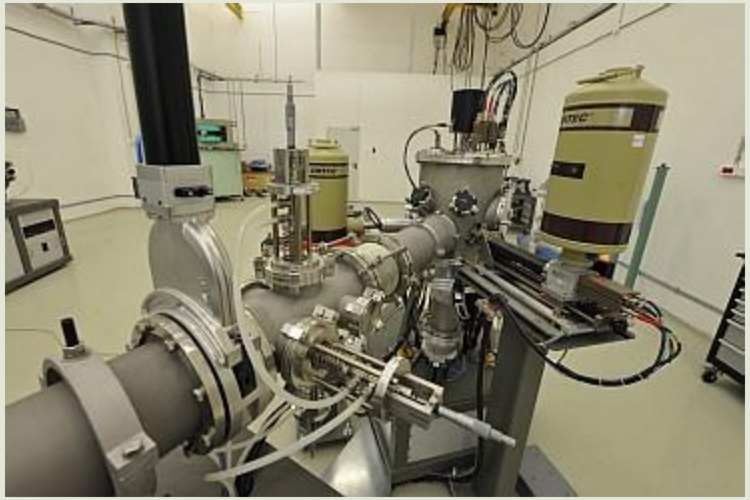
Experimental

The measurements have been performed at the **3MV Tandetron of IFIN-HH, Magurele, Romania**

https://tandem.nipne.ro/applied_physics.php

https://tandem.nipne.ro/3MV_Tandetron.php

The 3 MV Tandetron accelerator was installed in 2012 and is mainly dedicated to applied physics experiments. The machine is fully equipped to do ion beam analysis (IBA) and implantation experiments. The first beam-line has all the necessary detectors to perform particle induced X-ray emission (PIXE), particle induced gamma ray emission (PIGE), Rutherford backscattering (RBS) and elastic recoil detection analysis (ERDA).



Detectors employed:

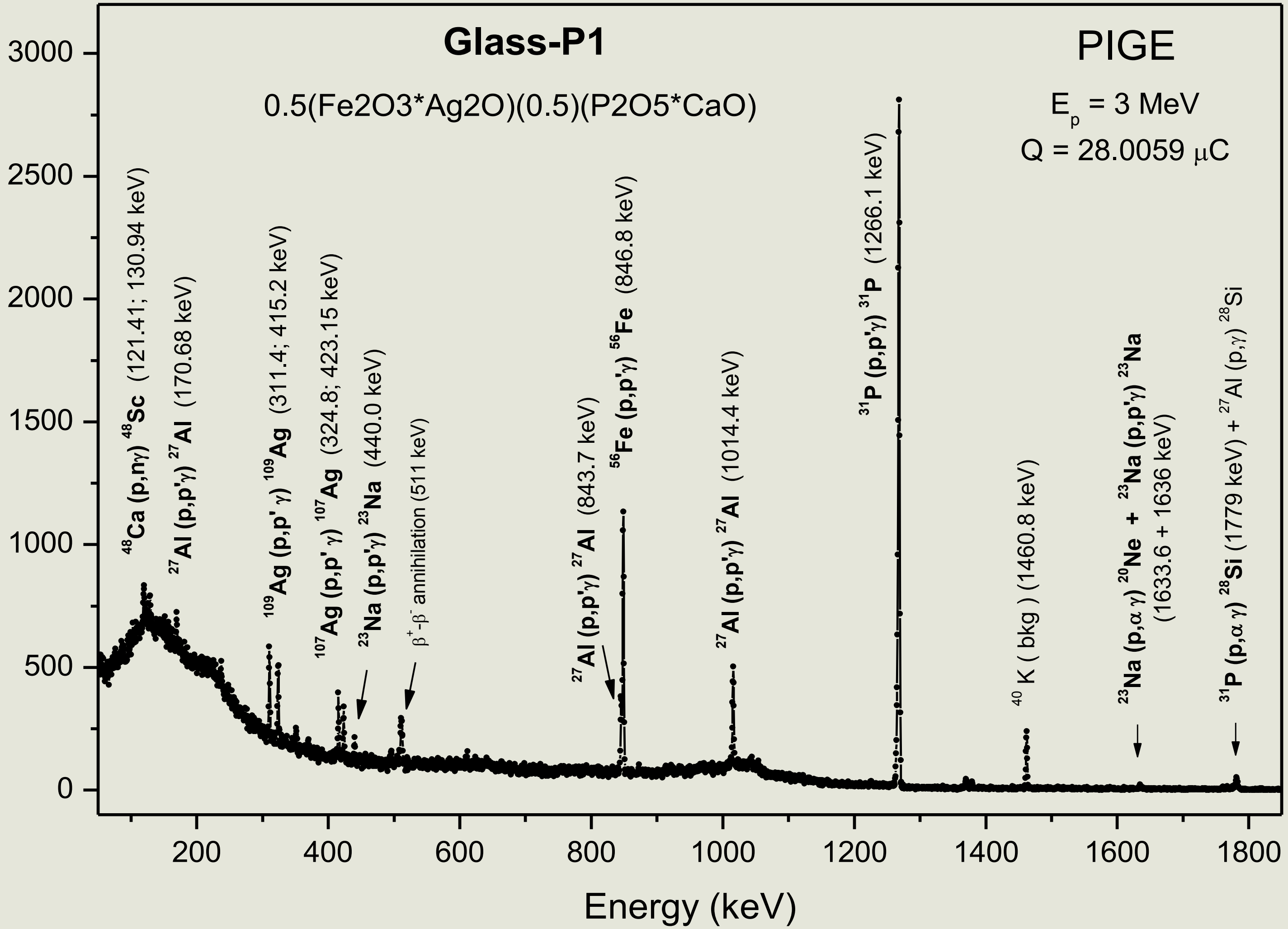
- Silicon Drift Detector (SDD) Amptek of 25 mm2 x 500 µm and Be window of 0.3 mil for **PIXE** (external beam) .

- HPGe Ortec detector of 10 % relative efficiency and 1.75 keV FWHM at 1332 keV of 60Co for **PIGE**.

- A passivated ion implanted Si detector with energy resolution of 16 keV for **RBS**.

Particle Induced Gamma Emission (PIGE)

Proton internal beam in vacuum (3 MeV)
Thick targets



Elements determined by PIGE :

Fe, Ag, P, Ca (major elements), as well as **Al, Na.**

Nuclear reactions:

^{56}Fe (p,p´g) ^{56}Fe (846.8 keV)
^{57}Fe (p,p'γ) ^{57}Fe (122,1; 352,4 keV)

^{109}Ag (p,p'g) ^{109}Ag (311.4; 415.2 keV)
^{107}Ag (p,p'g) ^{107}Ag (324.8; 423.15 keV)

^{31}P (p,p'g) ^{31}P (1266.1 keV)

^{48}Ca (p,nγ) ^{48}Sc (121,4; **130,9**; **370,3;** 1157 keV)

^{27}Al (p,p'g) ^{27}Al (843.7; **1014.4** keV)

^{23}Na (p,p'γ) **^{23}Na** (**440;** 1636 keV)
^{23}Na (p,αγ) **^{20}Ne** (1633.6 keV)

Particle Induced Gamma Emission (PIGE)

Proton internal beam in vacuum (3 MeV)

Thick targets

For PIGE standardization, a relative analytical method was applied with standards of certified element concentration, using the following formula:

$$C_{sample} = \frac{Y_{sample} \cdot S_{sample}(E_{1/2})}{Y_{standard} \cdot S_{standard}(E_{1/2})} \cdot C_{standard}$$

where, C_{sample} and $C_{standard}$, are the element concentrations (mass fractions) in sample and standard, respectively;

Y_{sample} and $Y_{standard}$, are element gamma-ray yields for sample and standard, respectively, normalized to the beam charge of the incident protons;

S_{sample} and $S_{standard}$, are stopping powers for proton beam of energy $E_{1/2}$, calculated using SRIM simulation program.

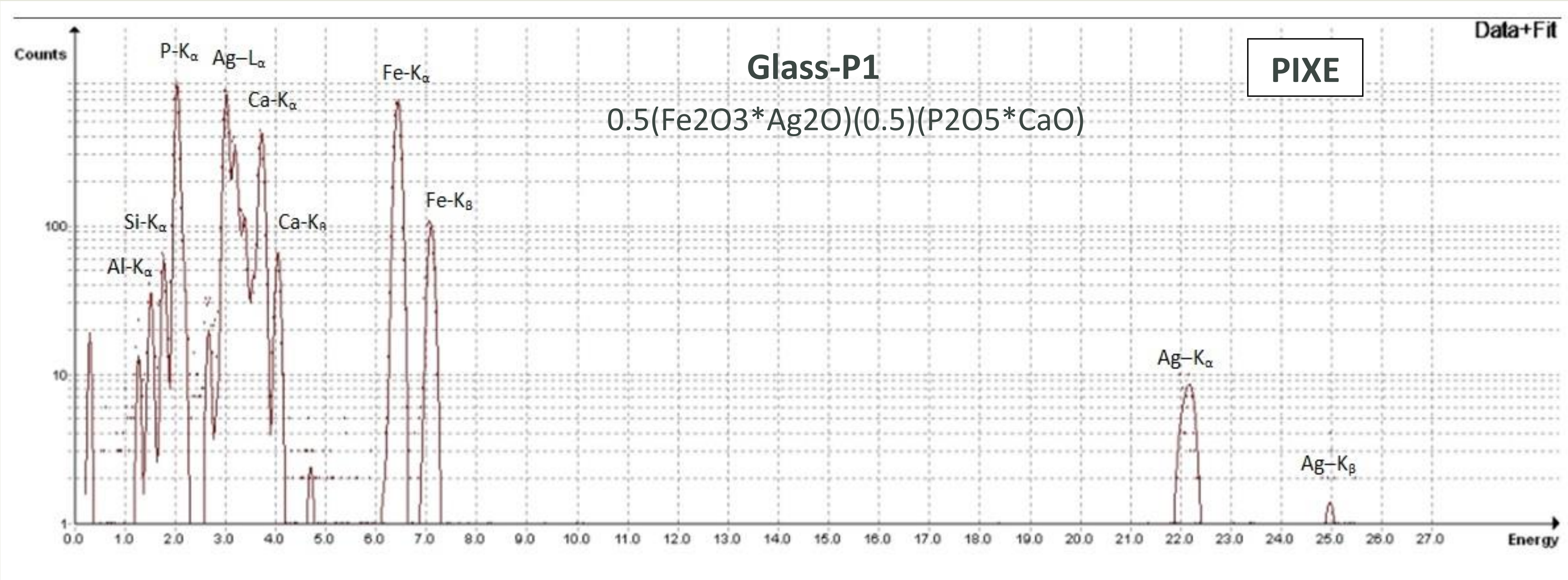
To determine $E_{1/2}$ (proton beam energy for which a halved reaction yield is observed), excitation functions were measured both for the investigated samples and comparator standards, in the beam range between 2.4 and 3 MeV.

As comparator standards, high purity Ag, Fe, and Al foils, as well as Fe_2P, $CaSO_4$ and NaCl chemical compounds were considered to determine Ag, Fe, Al, P, Ca, and Na.

Particle Induced X-ray Emission (PIXE)

Proton external beam (2.830 MeV)

Thick targets



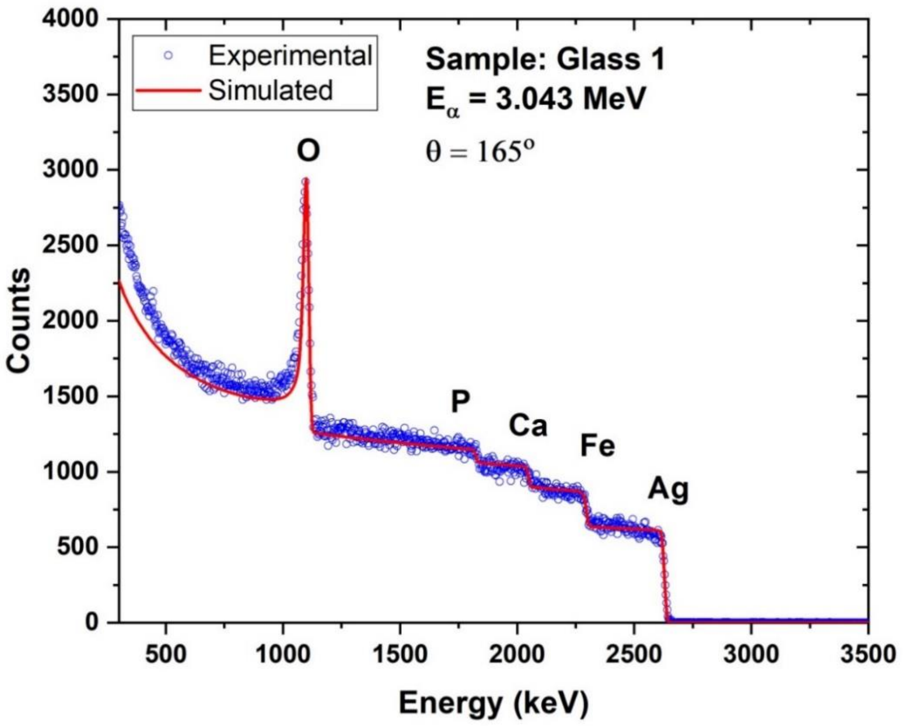
For PIXE analysis, GUPIX (Guelph PIXE) software was used. Energy calibration factors were determined using metallic foils (e.g. Al, Ti, Fe, Ni, Cu, Ag) of certified content. GUPIX fit for the Glass-P1 sample is here presented.

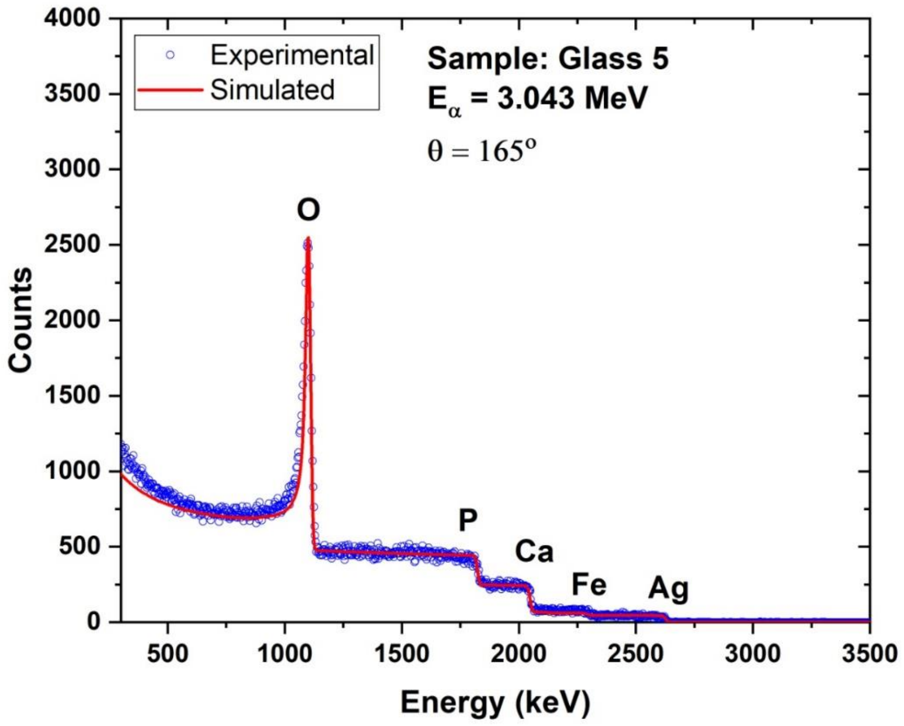
Elements determined by PIXE: Fe, Ag, P, Ca (major elements), as well as Al, Si, Mg, and Na trace elements.

Rutherford Backscattering Spectrometry (RBS)

Alpha internal beam in vacuum (3.043 MeV)

Thick target





For RBS, alpha particles of energy close to the resonance energy of 3.034 MeV for the ^{16}O scattering was chosen. The element contents in samples, normalized to 100 % total, were determined using SIMNRA software.

Elements determined by RBS: Fe, Ag, P, Ca, O (major elements).

Rutherford Backscattering Spectrometry (RBS)

Alpha internal beam in vacuum (3.043 MeV)

Thick target

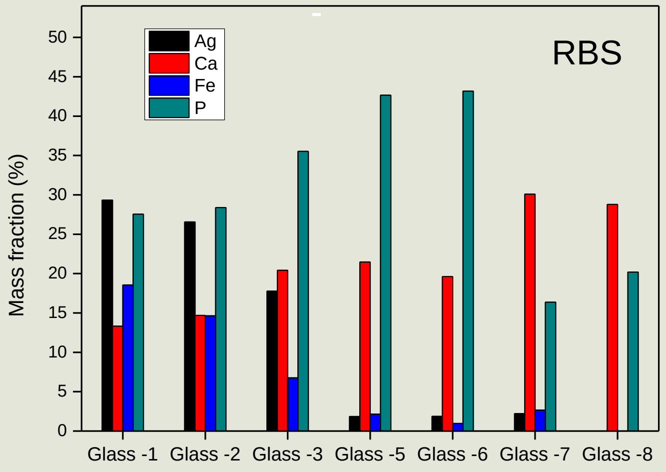
Elemental composition of the $x(Fe_2O_3*Ag_2O)(1-x)(P_2O_5*CaO)$ glass samples determined by RBS*

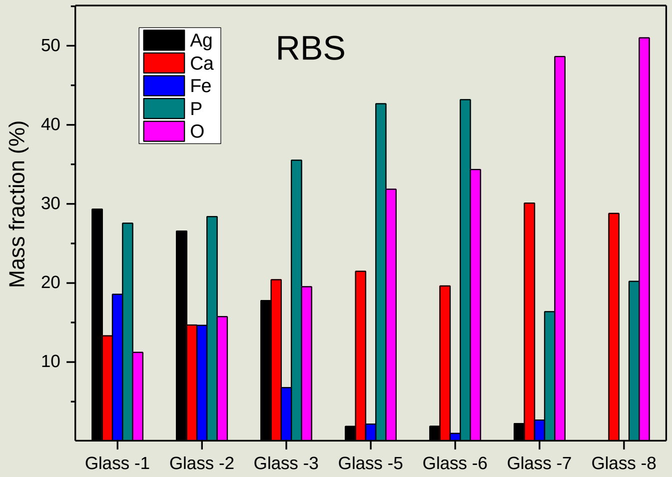
Composition stoichiometry

Sample	Ag	Ca	Fe	O	P
Glass -1	0.090	0.110	0.110	0.570	0.120
Glass -2	0.078	0.116	0.083	0.562	0.161
Glass -3	0.045	0.139	0.033	0.611	0.172
Glass -5	0.004	0.125	0.009	0.622	0.240
Glass -6	0.004	0.113	0.004	0.623	0.256
Glass -7	0.006	0.220	0.014	0.300	0.460
Glass -8		0.198		0.348	0.454

Elemental mass fraction

Sample	Ag (%)	Ca (%)	Fe (%)	O (%)	P (%)
Glass-1	29.33	13.32	18.56	27.55	11.23
Glass-2	26.56	14.68	14.63	28.39	15.74
Glass-3	17.78	20.41	6.76	35.52	19.53
Glass-5	1.85	21.48	2.15	42.66	31.86
Glass-6	1.87	19.62	0.97	43.19	34.35
Glass-7	2.21	30.10	2.67	16.38	48.64
Glass-8		28.79		20.20	51.01

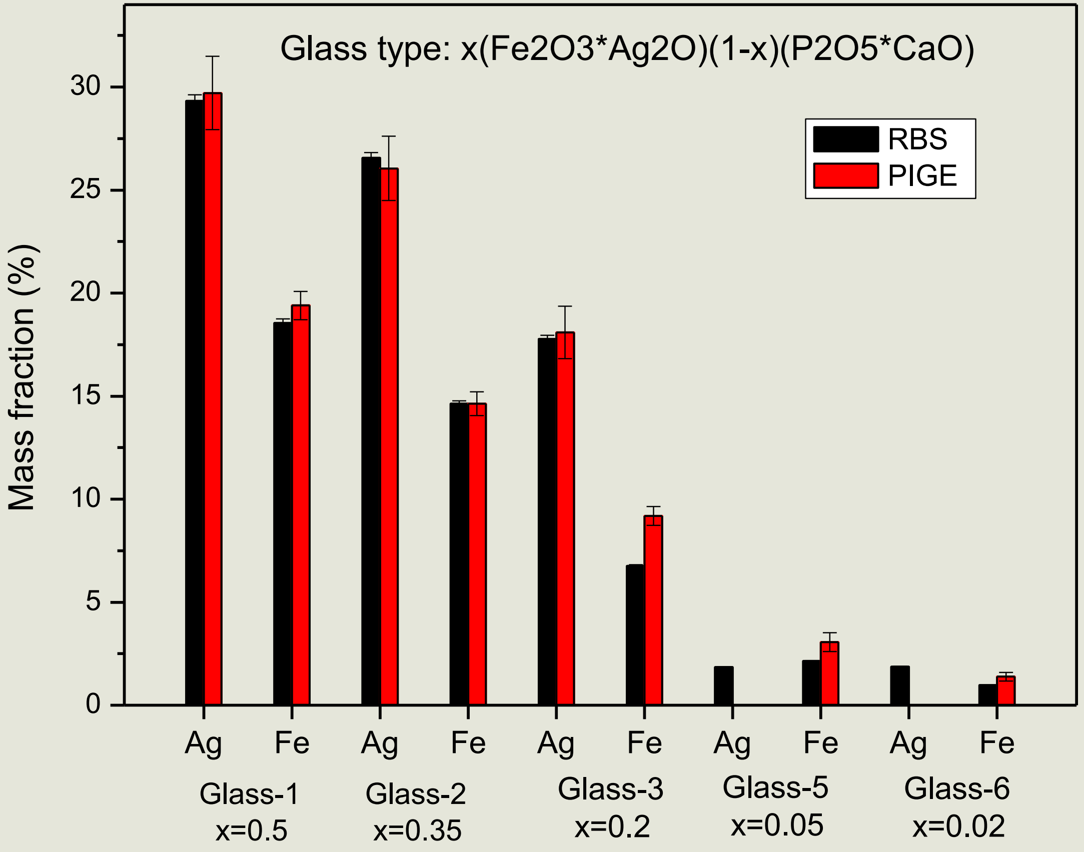




* SIMNRA software home page: http://www.simnra.com

RBS and PIGE analytical results for Fe and Ag

x(Fe2O3*Ag2O)(1-x)(P2O5*CaO) glass samples



The results obtained by PIXE, PIGE and RBS for the major elements Ag, Ca, Fe and P in the investigated glass samples were found to be in a good agreement.

Elemental contents of the glass samples are lower than 30 % and 19 % for Ag and Fe, respectively, being situated in the ranges 11-51 % for P, and 13-30 % for Ca.

A comparison of the RBS and PIGE results for Ag and Fe in five glass samples is here presented.

Analytical uncertainties for PIGE are of 3-5 % for P, 3-25 % for Fe, 7 -30 % for Ag, and 15-20 % for Ca. Detection limits (LD) of 0.7 % for Fe and 3 % for Ag were determined.

Conclusions

- New $x\left(Fe_2O_3 \cdot Ag_2O\right) \cdot (100-x)\left[P_2O_5 \cdot CaO\right],\ 0 \le x \le 0.5$ glass systems have been prepared and detailed investigations of the resulted composition are necessary.
- For the confirmation of the compounds composition and stoichiometry the PIXE, PIGE and RBS measurements were employed.
- Besides major elements determined by RBS (P, Ca, Fe, Ag and O), as well as PIXE and PIGE (P, Ca, Fe, and Ag), minor and trace impurity elements (e.g. Na, Mg, Al, Si) could be measured by PIXE and PIGE complementary techniques for the optimization of the preparation methodology.
- The results obtained by PIXE, PIGE and RBS for the P, Ca, Fe, and Ag major elements in the investigated glass samples were found to be in a good agreement.

Thank you for attention!