s12.m34.p3 **Neutron Diffraction Study and RMC Modelling of Borosilicate Matrix Glasses.** M. Fábián[1], E. Sváb, Gy. Mészáros[1], L. Kőszegi[1], E. Veress[2], [1]*Research Institute for Solid State Physics and Optics, H-1525, Budapest POB 49. Hungary,* [2]*Babes-Bolyai University, Faculty of Chemistry, 11 Arany János St., RO-3400 Cluj, Romania. E-mail: fabian@szfki.hu*

Keywords: Borosilicate glasses; Neutron diffraction; RMC

Borosilicate glasses are of significant current interest as suitable materials for isolating host media for radioactive waste materials [1,2]. We have undertaken a systematic structure investigation on a newly synthesized borosilicate based matrix glass system of general formula of mole%

$(65\text{-}x)SiO_2$*25 Na_2O*5BaO*5B_2O_3*xZrO_2 ($0 \le x \le 5$) and CeO_2 for simulation of radioactive PuO_2. As Ce and Pu coordination in complex oxide environments is similar, we expect that the Pu coordination will be properly simulated by CeO_2 addition in the host glasses. The samples were prepared by melting in platinum crucible at 1300-1450 °C, working in atmospheric conditions.

Neutron diffraction measurements were performed at the 10 MW Budapest research reactor using the 'PSD' and 'MTEST' neutron diffractometers [3]. Despite of the great hydrolytic stability of the samples, the first few experiments revealed their tendency to superficially adsorb H_2O. Atmospheric humidity caused a surface swelling of the air-kept samples, and the hydrogen contained by the hydrolysed layer produced great incoherent scattering. The samples were dried at 120 C for 4 hours under vacuum conditions, which proved to be completely sufficient to obtain neutron diffraction pattern adequate for data treatment.

For data evaluation both the traditional direct Fourier-transformation, and the reverse Monte Carlo (RMC) simulation methods were applied. As a result, we have obtained the partial atomic pair correlation functions for these multi-component glasses, making possible to determine first neighbour atomic distances and coordination numbers. For RMC starting model a disordered atomic configuration was build up. The convergence of the RMC calculation was good inspite of the extremely high number of simulated parameters, and the final fit matched very well the experimental structure factors. We could successfully calculate the different atomic distances of the glass network, i.e. Si-O and B-O distances at 1.4 and 1.7 Å, respectively, the discrete values of Si-B, Si-Na, B-Na, O-O, O-Na and Ba-Na distances around 2.6 Å, and the further neighbours up to 4.5 Å.

The work was supported by OTKA-T42495.

[1] W.G.Ramsey, N.E.Bibler and T.K.Meaker,"*Composition and durabilities of glasses for immobilization of plutonium and uranium*", Proc. WM95, University of Arizona, 1995.
[2] Donald, I.W., Metcalf, B.L. and Taylor, R.N.J., *Journal of Material and Science*, **32**, 5851 (1997)
[3] http://www.bnc.hu/

s12.m34.p4 **X-ray Study of Modulated BiMeVOXes (Me= Cu, Ni, Mg, Zn) Single Crystals.** Anna Gagor[a], Adam Pietraszko[a], Franciszek Krok[b], [a]*Institute of Low Temperature and Structural Research Polish Academy of Science, Wroclaw, Poland,* [b]*Institute of Physics, Warsaw University of Technology, Poland. E-mail: a.gagor@int.pan.wroc.pl*

Keywords: Oxide ion conductors; Modulated structure

The BiMeVOX family of fast oxide ion conductors has recently received much attention due to their excellent conduction properties at relatively low temperatures [1]. The parent compound of this family $Bi_4V_2O_{11}$ contains intrinsic oxygen vacancies and exhibits the polymorph phase transitions from highly conducting tetragonal γ phase to monoclinic or orthorhombic a phases and also orthorhombic β phase, with transition temperatures α - β, β - γ at about 400°C and 600°C, respectively. Substitution of isovalent or aliovalent cations Me for V can suppress the transition and stabilize the α, β or the γ type phases to room temperature. The g phase for the divalent substituted systems generally occurs between $x \approx 0.10$ to 0.13 [2] and reveals weak additional peaks that are attributed to an incommensurate modulated γ' superstructure. In the present paper have been shown the X-ray studies of the single crystal structures of four partially Mg, Zn, Cu and Ni substituted compounds: $Bi_4V_{2(1-x)}Me_{2x}O_{11-3x}$, Me = Ni, Mg, Zn; x = 0.1. The crystal structures of the compounds were examined from 150K to 490K using the "Xcalibur" diffractometer with area CCD detector. The JANA 2000 program [3] was used for structural refinement. Previous diffraction studies of BiMeVOXes were only concerned with it's average atomic structure or speculated on the existence of a domain structure with an orthorhombic deformation of the tetragonal structure. The present study is the first attempt to describe BiMeVOXes as a modulated structure in four dimensional superspace. The reconstruction of the reciprocal space showed that non-indexed reflections could be interpreted as first order satellites with the modulation vectors $\mathbf{q}=0.385\mathbf{a}^*$ and $\mathbf{q}=0.4\mathbf{a}^*$ for BiMgVOX and BiZnVOX respectively. Analysis of systematic absences implaied Fmmm(α, 0, 0)0s0 superspace group for both BiZnVOX and BiMgVOX compound. The X-ray diffraction patterns of BiCuVOX resemble the tetragonal γ' phase. Satellite reflections can be indexed by modulation vector $\mathbf{q}=0.31(\mathbf{a}^*+\mathbf{b}^*)$. As far as BiNiVOX is concerned X-ray diffraction patterns can be indexed in the γ phase, however the reciprocal space reconstructions reveal very weak satellite spots which indicate γ' phase. Intensity of this additional reflections is to weak to determine modulation vector. The details of redetermination of the crystals structure and data analysis and evaluation are discussed in the work.

[1] I. Abrahams, J.A.G Nelstrop, F. Krok, W. Bogusz *Solid State Ionics* **110** (1998) 95-101.
[2] I. Abrahams, F. Krok *Journal of Materials Chemistry*, **12** (2002) 3351-3362.
[3] V. Petricek, M. Dusek (2000). JANA2000. Institute of Physics, Praha, Czech Republic.