Iron phosphate glasses have been identified as an excellent candidate for immobilization of nuclear waste due to their excellent chemical durability, low melting temperatures and short melting times. In some instances, iron phosphate glasses may be more technically suitable and less expensive than the borosilicate glasses currently being the only material used to vitrify certain types of wastes. This is especially true for those wastes containing significant amount of Cr\textsubscript{2}O\textsubscript{3} which is poorly soluble in most borosilicate glasses so the waste loading is low and radioactive volume is undesirably large.

The aim of the present study was to investigate glass-forming ability and structure of iron phosphate glasses doped with high amount of Cr\textsubscript{2}O\textsubscript{3}. For that purpose two series of glasses, xCr\textsubscript{2}O\textsubscript{3}-(100-x)[40Fe\textsubscript{2}O\textsubscript{3}-60P\textsubscript{2}O\textsubscript{5}] and xCr\textsubscript{2}O\textsubscript{3}-(28.3-x)PbO-28.7Fe\textsubscript{2}O\textsubscript{3}-43.0P\textsubscript{2}O\textsubscript{5}, were prepared by melting and quenching technique. Appropriate mixtures of reagent grade: NH\textsubscript{4}H\textsubscript{2}PO\textsubscript{4}, Fe\textsubscript{2}O\textsubscript{3}, PbO and Na\textsubscript{2}CrO\textsubscript{4} were melted between 1373 and 1473 K for 2h in air in high purity alumina crucibles. The melt was quenched in air by pouring it into a steel mould to form rectangular bars, which were annealed for 3 h at 720 K. The structural changes in glasses were investigated by Raman spectroscopy, X-ray diffraction analysis (XRD) while microstructure was characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The samples were gold coated for SEM measurements. The differential thermal analysis (DTA) was used to study glass forming and crystallization characteristics.

The Raman spectra of Cr\textsubscript{2}O\textsubscript{3}-Fe\textsubscript{2}O\textsubscript{3}-P\textsubscript{2}O\textsubscript{5} glasses show that addition of <10 mol\% Cr\textsubscript{2}O\textsubscript{3} does not produce any changes in glass structure which is dominantly pyrophosphate. However, glass containing 10 mol\% of Cr\textsubscript{2}O\textsubscript{3} shows partial crystallization which is observed in sharp Raman bands and confirmed by XRD. The XRD pattern contains lines related to CrPO\textsubscript{4} and unidentified lines that cannot be matched with any existing XRD data available in the powder diffraction database. The SEM micrograph of partially crystallized glass shows well defined randomly distributed crystals embedded in homogenous glass matrix, Figure 1b. Furthermore, the SEM micrographs of partially crystallized Cr\textsubscript{2}O\textsubscript{3}-PbO-Fe\textsubscript{2}O\textsubscript{3}-P\textsubscript{2}O\textsubscript{5} glasses show complex surface microstructure. In comparison to homogenous glass matrix observed in 10Cr\textsubscript{2}O\textsubscript{3}-30Fe\textsubscript{2}O\textsubscript{3}-60P\textsubscript{2}O\textsubscript{5}, SEM micrograph of partially crystallized 4Cr\textsubscript{2}O\textsubscript{3}-24.3PbO-28.7Fe\textsubscript{2}O\textsubscript{3}-43.0P\textsubscript{2}O\textsubscript{5} glass shows phase separated glass matrix with well defined needle shape crystals located inside the holes, Figure 2c. The strong tendency toward phase separation in these glass series can be anticipated from the competitive strong field strengths of phosphorous and lead which causes melt to exhibits liquid – liquid immiscibility and results in phase separated glasses.
Figure 1. SEM micrographs of a) 10Cr$_2$O$_3$-30Fe$_2$O$_3$-60P$_2$O$_5$ and b) 4Cr$_2$O$_3$-24.3PbO-28.7Fe$_2$O$_3$-43.0P$_2$O$_5$ partially crystallized glasses.

Figure 2. AFM micrographs of 10Cr$_2$O$_3$-30Fe$_2$O$_3$-60P$_2$O$_5$ partially crystallized glass.

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