ESRF	**Experiment title:** Short-range and medium-range order in amorphous geopolymers analyzed by pair distribution functions	**Experiment number**: HC-2649
Beamline: ID22	**Date of experiment**: from: 26.09.2016 to: 29.09.2016	**Date of report**: 22.12.2016
Shifts: 6	**Local contact(s)**: Catherine Dejoie	*Received at ESRF:*

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Report:

Geopolymers based on metakaolin, a thermally treated kaolin clay, exhibit very promising properties as a potential nuclear waste form. By total scattering and pair distribution function (PDF) analyses we anticipated to get new insights into the structure of dominantly amorphous geopolymers on the atomic length scale. Together with results of Raman, IR, and MAS-NMR spectra a detailed picture of the geopolymers' network and its crystallographic features shall be drawn.

We investigated geopolymers of 14 different compositions containing Cs, Sr, Rb, K, Na or in combination ($K_{1-x}Cs_x$), ($Rb_{1-x}Cs_x$) or ($Ca_{1-x}Sr_x$) with x = 0.25, 0.50, and 0.75, respectively. For each of these compositions an amorphous and two thermally treated samples heated to 150 °C or 1150 °C were prepared. The geopolymer samples that crystallized during the thermal treatment at 1150 °C served as reference for the identification of interatomic distance correlations. The powdered samples were filled into Kapton tubes provided by Goodfellow with an inner diameter of 0.5 mm and 25 µm wall thickness. For higher intensities and better counting statistics 65 keV were used. The samples were rotated with 787 rpm and acquisition time for each sample was about half an hour. Subsequent data processing was conducted using PDFgetX3, where the absolute value of the scattering vector Q was restricted to the range of 0.53 $Å^{-1}$ to 27 $Å^{-1}$.

The total pair distribution functions G(r) of all geopolymers that cured at room temperature show very similar characteristics meaning similar peak positions as shown in figure 1. Also the degree of order is equal for the geopolymers with alkaline metal cations (Na, K, Rb, Cs), whereas the Sr-geopolymer shows a higher degree of order. All samples show a well defined short-range order up to 5 Å, but only the Sr-geopolymer exhibits also a long-range order, while the other geopolymers have only a weak medium-range order between 5 Å and 8 Å.

Marked r-values in the plot are lengths that can be correlated with interatomic distances appearing typically in aluminosilicates like pollucite and its analogues, or kaolin. For example, the strong signal at 1.63 Å can be attributed to T–O bonds with T = Si, Al in tetrahedral silicate and aluminate groups. The much weaker signal at 1.90 Å, that is partly superposed with the previous signal, corresponds to the Al–O distance in an AlO_6 octahedron. The O–O distance known from pollucite can be found at 2.67 Å. The following two broad signals at 3.00 Å and 3.24 Å can be interpreted as Si–Si, Al–Al, and Al–Si distances, explaining also the overlap of the signals. Additionally the distance between oxygen and the alkaline metal or alkaline earth metal cation should be located around 3.3 Å. Following rather broad humps around 4 Å and 5 Å correspond to the distances between the cation to Si and Al or between the cations among each other, respectively.

In contrast to the alkaline metal geopolymers, the geopolymers with the alkaline earth metal cations Ca and Sr (figure 2) have already crystallized at room temperature while nearly the complete water content

evaporated after opening the vials that served as sample containers. For these samples a long-range order up to 30 Å is observed, although it gets lost for the geopolymers with 50 % and more Ca on the cation position. In figures 3 and 4 the total pair distribution functions G(r) for the geopolymers with mixed cation compositions are plotted. The curves reveal a continuous change of intensities between the end members, while the peak positions and the general curve shapes have significant similarities.

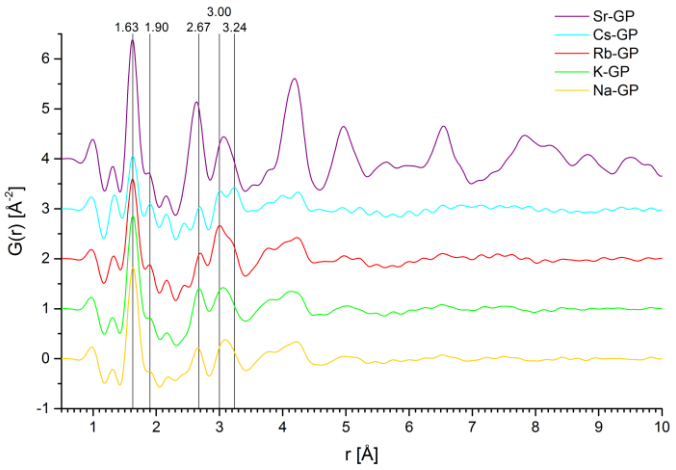

Figure 1: Total pair distribution function G(r) of geopolymers (GP) with the four different alkaline metal cations Na, K, Rb, and Cs as well as a geopolymer with the alkaline earth metal cation Sr. Marked r-values can be correlated to interatomic distances that can be found in the crystal structure of pollucite and its analogues.

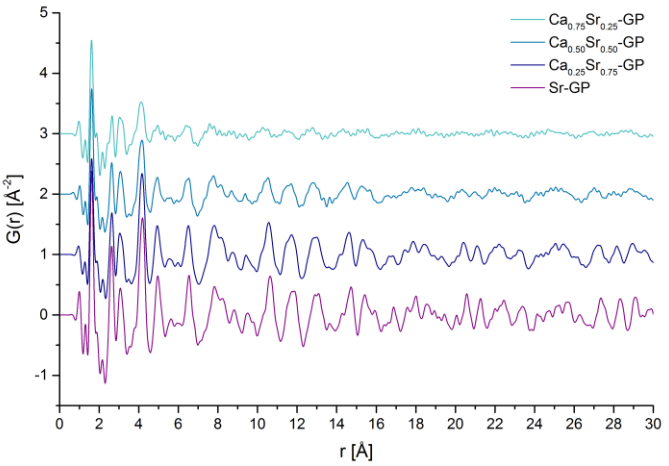

Figure 2: Total pair distribution function G(r) of ($Ca_{1-x}Sr_x$)-geopolymers. Fluctuating intensities up to 30 Å indicate a distinct long-range order.

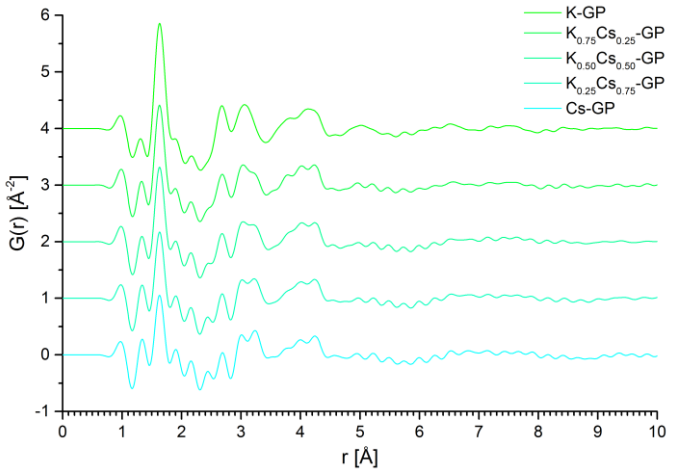

Figure 3: Total pair distribution function G(r) of ($K_{1-x}Cs_x$)-geopolymers.

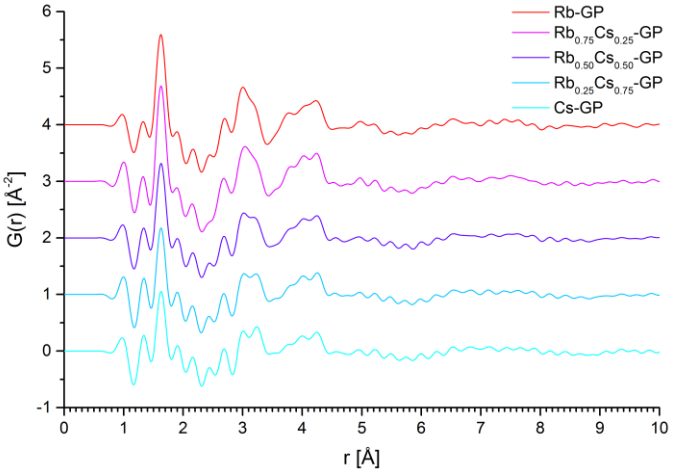

Figure 4: Total pair distribution function G(r) of ($Rb_{1-x}Cs_x$)-geopolymers.