

**MS24-P7** Investigating short-range order in transition-metal-bearing aluminosilicate garnets with  $^{27}\text{Al}$  and  $^{29}\text{Si}$  MAS-NMR spectroscopy: Using paramagnetic interactions to directly measure local atomic configurations

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The rich crystal chemistry of the garnet group is related to the presence of three crystallographic cation sites with different coordination environments into which a wide range of elements can substitute. Most natural silicate garnets with the general formula  $^{\text{VIII}}\text{X}_3^{\text{VI}}\text{Y}_2^{\text{IV}}\text{Si}_3\text{O}_{12}$  are solid solutions and they are important phases in Earth's crust and upper mantle. Thus, an understanding of their thermodynamic properties is important for petrogenetic modeling, but very little is known about one of the key thermodynamic terms, the configurational entropy. This term is determined by cation order-disorder, which can be both long and short-range in nature.

We present  $^{27}\text{Al}$  and  $^{29}\text{Si}$  Magic Angle Spinning Nuclear Magnetic Resonance (MAS-NMR) spectra for a suite of natural and synthetic pyrope-rich ( $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ ) and grossular-rich ( $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ ) solid solutions containing the paramagnetic transition metals  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ , and  $\text{V}^{3+}$ . The divalent cations can substitute at the X site and the trivalent cations at the Y site. The possibility of short-range order in the respective solid solutions is investigated.

The spectra show that paramagnetic interactions involving the unpaired electrons from  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$  only lead to peak broadening and loss of resolution of the  $^{27}\text{Al}$  and  $^{29}\text{Si}$  resonances. On the other hand, peak broadening from paramagnetic  $\text{Fe}^{2+}$  and  $\text{V}^{3+}$  is less severe, but for these species new paramagnetically shifted peaks having relatively large frequency shifts from the central resonances can be observed. These peaks are caused by  $\text{Fe}^{2+}$  or  $\text{V}^{3+}$  located at X or Y sites, respectively, that are greater than 5 Å away from the  $^{27}\text{Al}$  or  $^{29}\text{Si}$  nucleus. Taken together, such paramagnetically shifted peaks can provide a greater level of information concerning local structure (order/disorder) due to the fact that these peaks are sensitive to variations in site occupancy up to four atomic bonds away from the NMR active nucleus. NMR measurements, therefore, have the potential to measure the presence/absence of short-range ordering in transition-metal-bearing garnets and also a wide range of other materials. The spectroscopic results could complement structural information obtained from diffuse scattering measured in diffraction experiments.

**Keywords:** short-range order, NMR spectroscopy, mineralogy, garnet

**MS24-P8** Nanoparticle crystal formation by the solvent-assisted nanoparticle self-assembly probed *in situ* by the grazing-incidence small-angle X-ray scattering

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The self-assembled two- and three-dimensional arrays of colloidal nanoparticles have been extensively studied in the last decade as promising structures for applications in nanophotonics, plasmonics, photovoltaics, biotechnology, sensors and other fields. As these arrays may be viewed as nanoparticle crystals, usual crystallographic concepts may be adopted for their analyses. The solvent-assisted self-assembly is a very attractive method for preparation of nanoparticle crystals because of its simplicity and possibility to obtain various symmetries such as hexagonal, rhombohedral, face-centered cubic or body-centered cubic depending on the external drying parameters. However, little is known about the self-assembly kinetics itself that gives a key to tailoring the structure and thereby properties of the nanoparticle crystal. We report on a time-resolved study of the nanoparticle self-assembly into a high-quality nanoparticle crystal with the face-centered cubic crystallographic symmetry. The grazing-incidence small-angle X-ray scattering (GISAXS) at MINAXS beamline of the high-brilliance synchrotron radiation source Petra III (DESY) was employed to track kinetics of the solvent evaporation driven self-assembly on casting a colloidal drop of plasmonic silver nanoparticles of 6 nm diameter on a silicon substrate. The short-range (cumulative) disorder typical for paracrystal structures before the complete solvent evaporation at 300-350 s after the drop casting was found with the exception of a time window of 125-150 s where a highly regular transient phase with the long-range order was observed. It is attributed to interaction between the organic surfactant shells of the neighboring nanoparticles (oleic acid and oleylamine) getting into contact in presence of the solvent residua (toluene) to the end of the solvent evaporation. This results in a larger nanoparticle hydrodynamic diameter with a smaller dispersion and thus temporary improvement of the crystallization. Such a behavior, that has never been observed before, has direct impact on the quality of the resulting nanoparticle crystal and tailoring its properties. The support of the projects APVV-0308-11 and VEGA 2/0004/15 is acknowledged.

**Keywords:** colloidal nanoparticles, nanoparticle self-assembly, nanoparticle crystal, paracrystal model, GISAXS