ESRF	**Experiment title:** Ultrafast alloying of metal nanoparticles	**Experiment number**: MA706
Beamline: ID09B	**Date of experiment**: from: 01-04-09 to: 03-04-09	**Date of report**: 18-08-09
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Report:

The aim of the past experiment was to record the ultrafast lattice changes in metallic nanoparticles with different constituents, such as copper and gold. One particular aim is to detect the in-situ alloying during femtosecond laser excitation. From our earlier results with suspensions of pure gold nanoparticles of tuneable sizes we have obtained a rather complete view on the possible structure formation during the photoexcitation [1-3]. The most prominent is the heating and subsequent cooling of the particle lattice including temporally melting of the particles. The temperature history and as well the reaction of the environment can be understood quantitatively and serve as a tool to anneal particles within a period less than a nanosecond.

Thereby chemically prepared particles can undergo a reordering of the lattice to eventually result in alloyed nanoparticles. The test case of copper-gold particles is of particular interest, as the bulk phase diagram is well understood with several ordered phases and order-disorder phase transitions. This system may serve as a test case for applying ultrafast annealing techniques for homogeneous nanoparticles of desired structure (such as in magnetic systems).

We have prepared mixed nanoparticles by the co-reduction of copper acetate and gold hydrochlorate with $NaBH_4$, which gave particle sizes after PVP stabilization and ripening between 20 and 30 nm diameter. These aqueous particle suspensions have been measured at ID09B with laser pump and x-ray probe techniques with a time resolution of 100ps. The suspension was pumped through the interaction area as an open jet. Thanks to the newly implemented Frelon CCD camera is was possible to take exposures with very short down time of detector reading and data storage, which simplified the handling of the jet.

One problematic thing is the less than optimal mode profile of the femtosecond pump laser, which made it difficult to achieve a homogeneous focus at the sample position. Such homogeneous focus is a prerequisite in our studies, since it is imperative to have a uniform temperature distribution of the heated nanoparticles across the x-ray focus area. By some lengthy tweaking with focussing and mode filters we achieved a acceptable focus. Additional installations, such as the spec controlled syringe pump went smoothly after getting help from M: Cammarata and L. Guerin.

Unfortunately there was a failure of the air conditioning in the experiment hutch, which shut down the laser system entirely. Thanks to L. Guerin's heroic work on realigning the laser at a complete different set point it was still possible to measure almost the entire sample material.
The technique was monochromatic wide angle scattering, which allowed to distinguish between the different crystallographic phases in powder scattering. As seen for the following figure 1, the gold (111) peak is the most prominent one, already showing that during the synthesis the phases are demixed. The gold peak can also serve as local thermometer, as its expansion directly after laser excitation defines the reached lattice temperature.

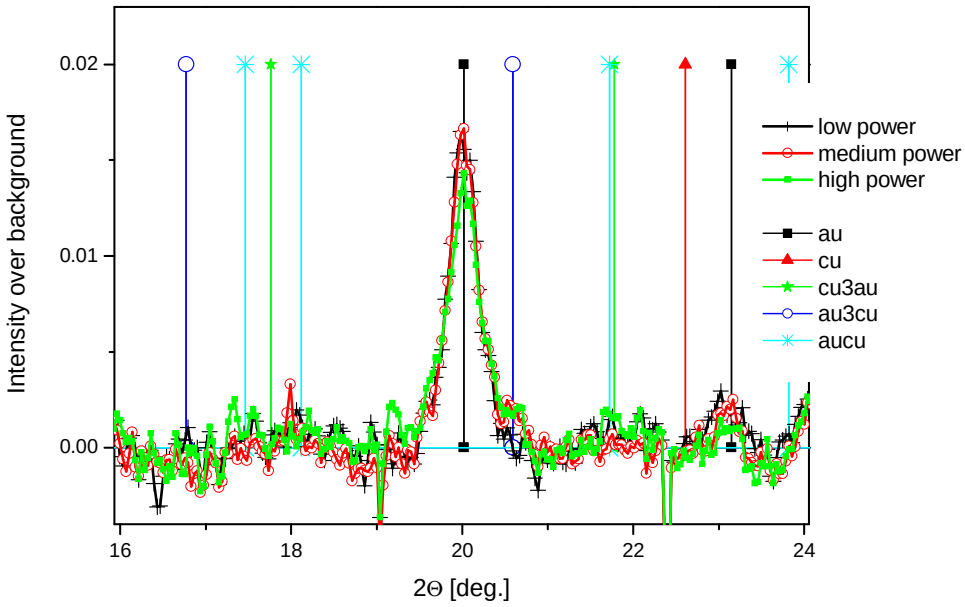

Fig. 1: Powder scattering of photo-excited copper-gold nanoparticles. The positions of putative alloy phases are indicated as vertical lines. The data is averaged for different laser fluence levels at a time delay of 1 µs, where the particles have completely cooled down.

Thereby we divided the laser power scale in 3 different regions, a low fluence region where the particle heating is much below the melting point (expansion typically < 1.2 %), a medium fluence region where the melting point os reached (expansion up to 1.8 %) and a high fluence region with complete melting of the particles. The scattering intensity is as well located as weak peaks around the different allow phases of Au_3Cu and possibly AuCu, both mostly for the fundamental (111) reflections. At the ordered structure peaks (100) and (110) barely any signal is visible. Concluding some alloy phase is formed despite the majority of separated gold phase.
This effect could stem from the rapid room temperature synthesis, which prohibits a formation of a gold-copper mixture. On the other hand a formation of amorphous alloys is predicted by Molecular Dynamics simulations by a theoretical work [5], which seems not to be in line with the present observations.

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[2] A. Plech, V. Kotaidis, K. Istomin, and M. Wulff, *J. Synchr. Rad.* **14**, 288, 2007.

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