MLF Experimental Report

課題番号 Project No. 2009A0054	提出日 Date of Report 2014/11/19
実験課題名 Title of experiment Cooperative dynamics in noble-metal halides superionic melts	装置責任者 Name of responsible person Dr. Kenji Nakajima
実験責任者名 Name of principal investigator Yukinobu Kawakita	装置名 Name of Instrument/(BL No.) BL14
所属 Affiliation Faculty of Sciences, Kyushu University (present affiliation: J-PARC Center, JAEA)	実施日 Date of Experiment 2009/12/10-12/15

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。（適宜、図表添付のこと）
Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

CuI in silica glass capillary

Silica

2. 実験方法及び結果（実験がうまくいかなかった場合、その理由を記述してください。）

Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

CuBr, CuI and AgI are well-known to exhibit the superionic behaviour in the high temperature solid state (α-phase), where the mobile cations migrate between the sites in the sublattice of immobile halogen ions [1]. On the other hand, CuCl, AgCl and AgBr have rocksalt structure [2] until their melting points which doesn't show superionic behavior except of gradually increasing ionic conductivity by Frenkel type defect just before melting. Such difference in ionic conduction among noble-metal halides may be originated from the bonding nature of unlike ion pair with imperfect charge transfer [1].

In the molten state, bonding character tends to be enhanced by the lack of long range order. Recently, by the Reverse Monte Calro (RMC) structural modeling based on experimental data both of X-ray and neutron diffractions, we found that the cation distributions of molten AgI and CuI are essentially different from that of molten AgCl. The former has large fluctuations and, when ions within 3.5 Å are conveniently bonded with each other in the RMC structural model, chain like stream can be found. The Cu-Cu pair correlation has a peak almost close to the nearest

2. 実験方法及び結果（つづき） Experimental method and results (continued)

neighboring shell of the unlike pair. The fluctuations in Cu distribution cause the existence of the first sharp diffraction peak (FSDP) around at 0.86 $Å^{-1}$ in cation-cation partial structure factor. The latter exhibits much uniform distribution but the cation-cation pair correlation is extremely flat gas-like structure without any peaks. As a result, we can categorize AgI and CuI as “superionic conducting melt” and AgCl and CuCl as “non-superionic conducting melt.” For CuBr, structural properties are intermediate, and it is expected that Cu ions in molten CuBr are in mixed motion between cooperative chain-like motion and individual motion like gas.

In this project, we planned to measure QENS for CuBr and CuI in the molten states and superionic α-phases by using AMTERAS spectrometer at BL14. The sample was sealed under vacuum into a thin walled quartz tube and inserted into a sample holder made of Nb foil. Since there was no furnace belonging to MLF or the beamline, we had to bring a furnace from KEK. This furnace was “1800C Furnace” with Nb foil heater element (the requirements: three phase electrical source with 200V and 50A, and cooling water with 10 L/min) which is owned by KEK and was managed by the principal investigator who had been a leader of the instrumental group for LAM-40 spectrometer in KENS. Under the approval of KEK, it was brought from Tsukuba to Ibaraki Quantum Beam Research Center (IQBRC) to be examined by experts responsible to instrument safety in MLF. After the test run where enough high temperature was safely achieved, it was brought from IQBRC to the BL14 beamline by MLF staffs. To adjust the flange size and the depth of the scattering center at the BL14, a fitting flange was designed by the principal investigator and developed by KEK. After setting the furnace to the flange of BL14, the scattering contribution from the furnace itself was measured. We observed a large background and two elastic-like scattering streams both from the upward and downward of the scattering center, which might be caused by water tanks of the furnace vessel. During the first heating up with a silica glass capillary (the empty cell), the furnace was emergency stopped at around 200 °C with an alarm of wire-break signal. The instrument safety expert confirmed a break of the welded part between the electrode and the Nb heater foil and then the instrument group decided an interruption of this experiment. Since the test run at IQBRC had been succeeded, it is strongly inferred that the break of the heater element happened during the delivery from IQBRC to MLF or the mount process of the furnace to the neutron instrument, although damages might be accumulated during all procedure of transferring the furnace from Tsukuba to Tokai. The used beamtime was around one day. After that, we could not get the permission of utilization of that furnace and then gave up the experiment.