（ ※本報告書は英語で記述してください。ただし、産業利用課題として採択されている方は日本語で記述していただいても結構です。 ）

MLF Experimental Report

提出日 Date of Report	
課題番号 Project No. 2014A0178	装置責任者 Name of responsible person Toshiya Otomo
実験課題名 Title of experiment Structural fluctuation by mixed ionic conduction in superionic conductors and their molten phases and anion polarization effects	装置名 Name of Instrument/（BL No.） High Intensity Total Diffractometer (NOVA) / (BL-21)
実験責任者名 Name of principal investigator Shuta Tahara	実施日 Date of Experiment 2014.11.6 – 2014.11.10
所属 Affiliation University of the Ryukyus	

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.

(1) Copper Iodide – Silver Iodide mixture, $CuI_{0.8}AgI_{0.2}$

(2) Copper Iodide – Silver Iodide mixture, $CuI_{0.5}AgI_{0.5}$

(3) Copper Iodide – Silver Iodide mixture, $CuI_{0.2}AgI_{0.8}$

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.

Each powder sample of $(CuI)_x(AgI)_{1-x}$ was packed into a silica-capillary. We measured the neutron diffractions for the mixture samples at 450° C for superionic phase and 510° C – 670° C for molten phase. We used the vanadium furnace, which is equipped by the NOVA instrumental group, for the high temperature measurements.

Figure 1. shows the structure factor, $S(Q)$, for molten $(CuI)_{0.8}(AgI)_{0.2}$ mixture obtained by the experiment at BL-21, together with $S(Q)$ for pure molten CuI measured in another facility. A first sharp diffraction peak (FSDP) observed in $S(Q)$ for pure molten CuI at Q = 0.9 Å^{-1} is also observed for the molten mixture at same Q position as that for pure melt.

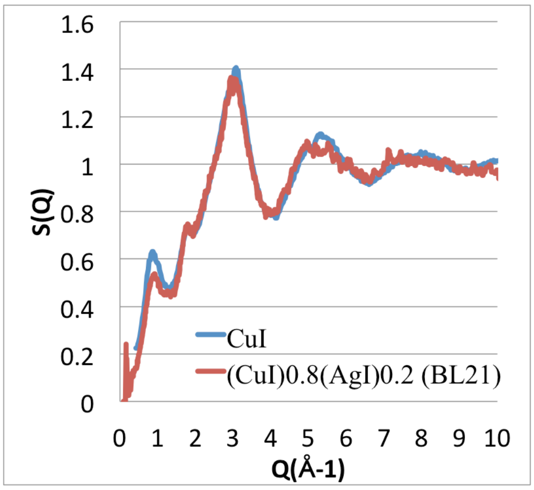

Fig. 1. S(Q) for molten CuI and $(CuI)_{0.8}(AgI)_{0.2}$ mixture.

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

It is confirmed that the height of the FSDP for the mixture is lowered by the replacement of Cu ions by Ag ions, indicating that the intermediate-range ordering of cations is affected by the replacements.

We performed molecular dynamics simulation on the mixture melt with the polarizable anion model. The partial structure factors, $S_{ij}(Q)$, and partial pair distribution functions, $g_{ij}(r)$, were obtained as shown in figure 2 and 3, respectively. $S_{CuCu}(Q)$ and $S_{AgAg}(Q)$ show the FSDP, indicating that Ag ions and Cu ions form intermediate-range ordering. Moreover, $S_{AgCu}(Q)$ also shows the FSDP, suggesting that Ag–Cu correlation has a intermediate-range ordering. In the case of pure superionic melts of AgI and CuI, the first peak of $g_{AgAg}(r)$ and $g_{CuCu}(r)$ penetrate into cation–anion first neighboring shell, which is originated from the covalent bonding between cations. The penetration of cation–cation correlation is also observed in the mixture. In particular, the penetration of Cu–Ag correlation suggests that the covalent bonding is formed between Cu and Ag ions, which may be the first discovery of the covalency between unlike–cation pairs in superionic melt.

We are now analyzing the intermediate–range ordering of cations and ionic transport properties in the mixture melt by voronoi–dealunay method and the calculation of mean square displacement, respectively. We intend to publish the experimental and theoretical results for international journals in near future.

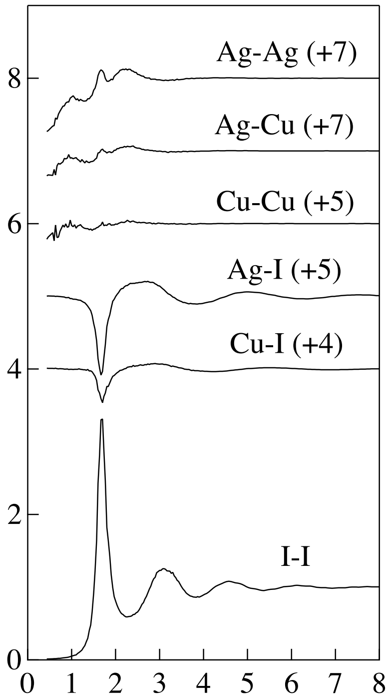

Fig. 2. $S_{ij}(Q)$ for molten $(CuI)_{0.8}(AgI)_{0.2}$.

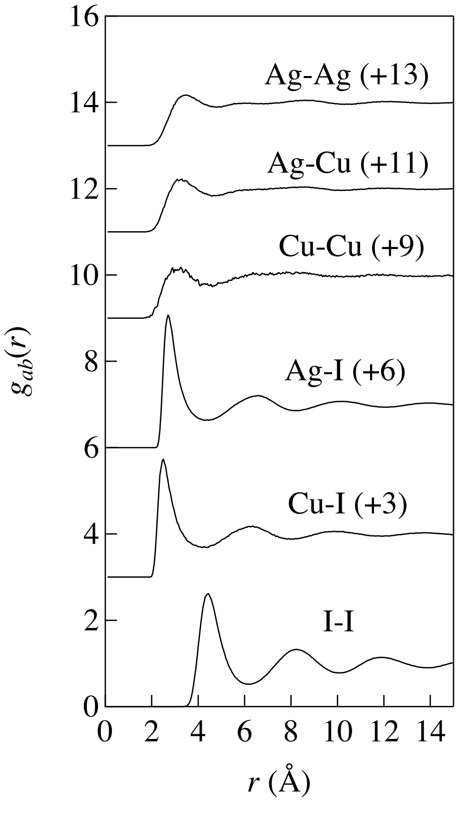

Fig. 3. $g_{ij}(r)$ for molten $(CuI)_{0.8}(AgI)_{0.2}$.