Anion induced-polarization effects on the local structure of molten silver halides

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AgI and CuI are well known to exhibit super-ionic conducting behavior at a high-temperature solid phase, where the mobile cations migrate between the sites in the sublattice of immobile iodine ions. Such property may result from the intermediate nature of cation-atomic bond between pure ionic and covalent one. The purpose of this project is to obtain the precise structure of molten noble-metal halides and discuss the bonding nature in the molten state in relation with the static structure. Especially we aim at deducing the partial structures with the aid of Reverse Monte Carlo (RMC) analysis and comparing with the earlier works. [1]

X-ray diffraction measurements for molten AgI and CuI were performed using high energy X-ray at 113.26keV at BL04B2. The sample was scaled in a quartz glass container with 3mm inner diameter and 0.4mm wall-thickness, which was located in the chamber filled with He 1atm gas. High temperatures were achieved by a Mo resistance wire of 0.4mm diameter.

Fig. 1 shows the structure factors, S(Q), for molten AgI and CuI. Both S(Q)\(\bar{3}\)s resemble to each other in the peak position. For molten CuI, partial structure factors, S\(\bar{3}\)(Q), have been deduced by RMC using XRD and ND data (see Fig. 2). The S\(\bar{3}\)(Cu)=Q) has a prepeak at 0.88Å\(\bar{3}\), while S\(\bar{3}\)(Q) has a quite sharp peak at 1.6Å\(\bar{3}\). The obtained model for molten CuI at 650°C is visualized in Fig. 3, where large and small spheres denote I and Cu ions, respectively. The Cu-Cu bonds are depicted by a stick for the Cu-Cu pairs in the distance less than 3.6Å. The Cu ions distribute with a large density fluctuation and several Cu ions lies in a quite short distance from each other, which may originate from the partial covalency of Cu-Cu pair as Shimoojo et al. recently pointed out from the ab initio MD simulation. [2]

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High Energy X-ray Diffraction Study of Liquid Structure of Metallic Glass Forming Zr\(_5\)Cu\(_{30}\) Alloy

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A high stability of deeply undercooled liquid state is an essential feature to form bulk metallic glasses with low critical cooling rates. The origin of this stabilization of undercooled state has been still mainly understood. The bulk glass forming in particular from microscopic point of view. Therefore, it is necessary to investigate the liquid structure of bulk glassy alloys as a function of temperature from the equilibrium liquid state to the supercooled region. Recently, various containerless techniques have been developed to accurately measure properties and structure of metallic melts at high temperatures. In this study, we have newly developed the conical nozzle levitation system combined with the two-axis diffractometer for high-energy synchrotron X-rays to obtain reliable diffraction data of metallic glass forming Zr\(_5\)Cu\(_{30}\) alloy in the liquid state.

The spherical sample (2mm) was prepared from pure constituent element by means of arc melting. The high-energy X-ray (113.6 keV) diffraction measurement was performed at BL04B2 beam line. The scattered X-rays were collected by the Ge solid-state detector. The covered range of the scattering angle, 2\(\theta\), in the present experiment was typically from 0.3° to 18°, which corresponds to the range of the momentum transfer, \(Q = (4\pi/\lambda)\sin(\theta/2)\), from 3 to 180 nm\(^{-1}\). The Zr\(_5\)Cu\(_{30}\) sample was levitated using highly purified Ar gas and melted with the use of CO\(_2\) laser. The temperature was kept at 100 K higher than the melting temperature during the diffraction experiment.

Fig. 1 shows the X-ray diffraction patterns obtained for levitated liquid Zr\(_5\)Cu\(_{30}\) alloy at 1453 K and for the background contributed mainly from Ar gas scattering. It can be seen that the intensity profile of background shows no significant contribution to that of the liquid sample due to the containerless condition. It is to be noted that a shoulder exists on the second peak in \(2\theta\) around 5°. This shoulder probably indicates an existence of local short range ordering in liquids. Detailed analysis with the use of Reverse Monte Carlo simulation is in progress.

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![Fig.1 Raw data of high energy x-ray diffraction patterns obtained for liquid Zr\(_5\)Cu\(_{30}\) alloy and the corresponding background.](image-url)