High-energy X-ray diffraction studies of room temperature molten salts at SPring-8 high-energy X-ray diffraction beamline BL04B2

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Room temperature molten salts (RTMS) have been the subject of intensive investigations probing the various properties pertinent to their potential for technological applications. Indeed the low melting point coupled with the complex temperature-composition dependence of the physico-chemical properties made these materials attractive for basic and applied research.

EMIC, 1-ethyl-3-methylimidazolium chloride ($C_6H_{22}N_2Cl$), is widely employed as a cationic source for room temperature molten salts. The combination of EMIC and aluminum trichloride [1] has been most extensively studied for practical applications such as organic reactions, batteries and metal depositions [2,3]. Recently, several low temperature ionic liquids have been prepared by combining EMI^+ cation with organic and inorganic fluoride anions, and their electrochemical behaviors have been investigated [4,5]. Hagiwara *et. al* have recently reported a series of alkylimidazolium fluorohydrogenate (XMIF 2.3HF, X = alkyl group) melts with high conductivities [6-8]. Their viscosity and conductivity obey Walden's rule like other RTMS. The structural analysis of the molten salts is necessary to elucidate the mechanism to reveal the high conductivity accompanied by the low viscosity of these salts.

X-ray diffraction experiment is one of the powerful probes for molten salts, especially combined with synchrotron radiation. It provides several advantages; high resolution in real space due to the wide range of scattering vector Q (= $(4\pi\lambda\sin\theta$, 2θ: scattering angle, λ: wavelength of photons), smaller correction terms (especially for absorption correction), reduction of truncation errors, and capacity for direct comparison between X-ray and neutron diffraction data.

SPring-8 bending magnet beamline BL04B2 with a bent crystal monochromator [9] makes the high-energy X-ray diffraction experiments of molten salts possible in the transmission geometry. Kohara *et. al* have developed a horizontal two-axis diffractometer for non-crystalline materials [10] (Fig. 1) at SPring-8 high-energy X-ray diffraction beamline BL04B2.

Figure 2 shows the total structure factors, $S(Q)$, of XF 2.3 HF (X= 1-methylimidazolium (MI), 1-propyl-3-methylimidazolium (PrMI), 1-butyl-3-methylimidazolium (BMI), 1-pentyl-3-methylimidazolium (PeMI), 1-hexyl-3-methylimidazolium (HMI)). The FSDP (First Sharp Diffraction Peak) shifts from Q = 1.65 Å^{-1} to 1.84 Å^{-1} with the increase in size of the *N*-alkyl group on the imidazolium ring. In addition, pre-peaks or shoulders are observed below FSDP for all the melts. Especially, pre-peaks are observed at Q = 0.35 Å^{-1} and 0.4 Å^{-1} for PeMIF 2.3 HF, HMIF 2.3 HF melts, respectively, indicating a strong influence of the alkyl group on the intermediate-range order.

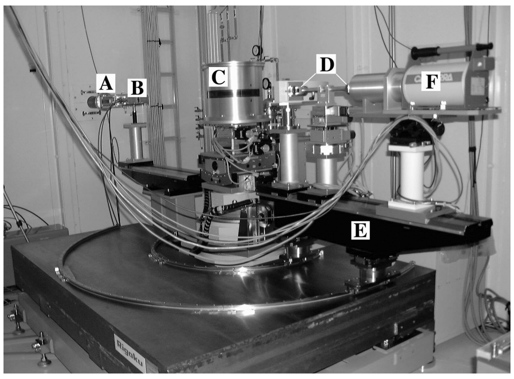

Fig. 1 A two-axis diffractometer for disordered materials installed at BL04B2 of SPring-8.
A: Be window, B: Ionization chamber, C: Vacuum chamber, D: Slit, E: 2*θ* arm, F: Ge detector

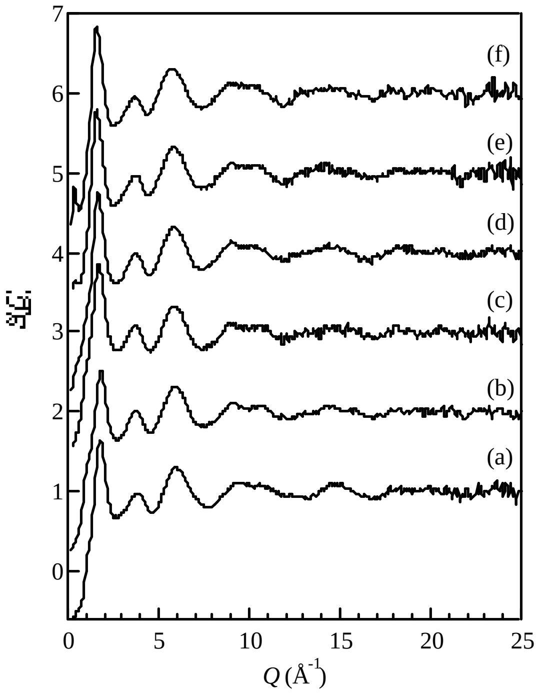

Fig. 2 The total structure factors, $S(Q)$, of XF 2.3 HF. (a) MIF 2.3 HF, (b) EMIF 2.3 HF, (c) PrMIF· 2.3 HF, (d) BMIF 2.3 HF, (e) PeMIF 2.3 HF, (f) HMIF 2.3 HF. Successive curves are displaced upward by 1 for clarity.

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