Photoirradiation effect on the ionic conductivity of β-AgI

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[Introduction] Silver iodide (AgI) is one of the most intensively studied ionic conductors. It exhibits at least six crystalline polymorphs and shows phase transitions by changing temperature and pressure. Although the photoresponse of the conductivity as well as the photoexcitation dynamics and its temperature dependence had been investigated for silver halides, the photoconductivity below 150 K and the possibility of the photoinduced phase transitions has been scarcely investigated for AgI. So far, we have investigated the control of the ionic conductivity in AgI by using light and external electric fields at room temperature.¹ In the present work, the photoswitching of the bulk resistance is investigated at 77K using complex impedance spectroscopy.

[Experimental] AgI pellets of diameter 13 mm and thickness 0.7-0.8 mm were prepared by pressing the grinded powder uni-axially at 200-250 kgf/cm². Then the pellets were immerged into potassium iodide (KI) solution for 2 days. To fabricate the electrodes on the surface of the pellets, carbon paste was used and the distance between the two parallel carbon electrodes was about 1-2 mm. The complex impedance spectra were measured with the ac voltage of 0.1 V in the frequency range from 5 MHz to 50 mHz using an impedance analyzer (Solartron, 1296+1260). A Xe lamp with intensity of 1x10⁻²W/cm² at 430 nm was employed as a light source for photoirradiation.

[Results and discussion] Fig. 1 shows the complex impedance spectra (Cole-Cole plot) of polycrystalline AgI before and after the KI treatment measured at room temperature. After KI treatment, the bulk resistance increased by more than one order of magnitude as the
percentage of the $\beta$-AgI component increased. Hereafter we call the sample as KI treated $\beta$-AgI. Fig. 2 represents the steady state normalized photocurrent excitation (PCE) spectra of KI treated $\beta$-AgI at 77 K measured by using dc method for the strong and weak intensities in the wavelength range of 700-300 nm. Photocurrent exhibits a sharp peak at 430 nm for both of the intensities but the photocurrent with strong intensity is about 10 times higher than that with weak intensity. Fig. 3 represents the complex impedance spectrum measured at 77 K. The bulk resistance of the KI treated polycrystalline $\beta$-AgI is in the giga-ohm range. However the bulk resistance decreases to the value in the sub mega-ohm range when the sample is irradiated with 430 nm. The change is more than two orders of magnitude and a gigantic photoinduced change in the bulk resistance is observed. After stopping the photoirradiation the bulk resistance cannot resume its original dark resistance. After 5 minutes we measured a different dark bulk resistance and with the increase of the waiting time the dark bulk resistance was increased but did not go back to its original dark resistance. The reversibility of the photoswitching phenomena between high and low resistive states at 77 K will be also discussed.

Reference