The study of electronic structure in ferroelectric semiconductor $Zn_{1-x}Li_xO$

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Zinc Oxide is *n*-type II-IV group compound semiconductor. ZnO have hexagonal structure with space group $P6_3mc$. Recentry, Onodera *et al* reported that ZnO have insulating and ferroelectric behaviour by lithium doped. Li doped ZnO are undergoes phase transition at 330 K with 6% dopant. The space group of Li doped ZnO is $P6_3mc$ as same as pure ZnO. The dielectric anomaly was reported about 30 at T_C=330 K with 6% dopant. The value is smaller than dielectric anomaly than typical ferroelectrics, for example $BaTiO_3$, KH_2PO_4. The transition entropy estimated form specific heat measurement was very small. Moreover, it is reported that the space group is kept $P6_3mc$ below T_C. These behaviour might indicate that the electronic structure arise the ferroelectric phase transition. In this study, the x-ray absorption spectroscopy (XAS) and x-ray emission spectroscopy (XES) was carried out by photon factory BL19b used synchrotron radiation, in order to elucidate the relation between the phase transition and electronic structure.

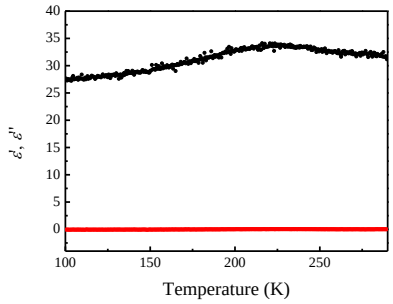

Figure1. Temperature dependence of dielectric measurement of Li 1.0 % doped ZnO at 1 MHz. The real and imaginary part of dielectric constant was shown black and red solid points.

The ceramics specimens were prepared by solid state reaction method at 1273K. Prepared specimens substituted Li for Zn with the ratio of 1%, 0.3%. Dielectric measurement was achieved, in order to estimation of phase transition temperature T_C. The XAS spectra were collected around 520 eV for excitation O2p from O1s. The excitation energy for XES was selected highest absorption energy from XAS spectrum. Temperature was controlled about 10 K for collection a spectrum on cooling.

The dielectric measurement of 1% doped ZnO was shown in Figure 1. The magnitude of the anomaly of real part is about 30 at 230 K. Thus, the phase transition temperature was estimated 230 K. The value of imaginary part is sufficient smaller than real part of dielectric constant whole all temperature reason. The dielectric anomaly was smaller and broader than

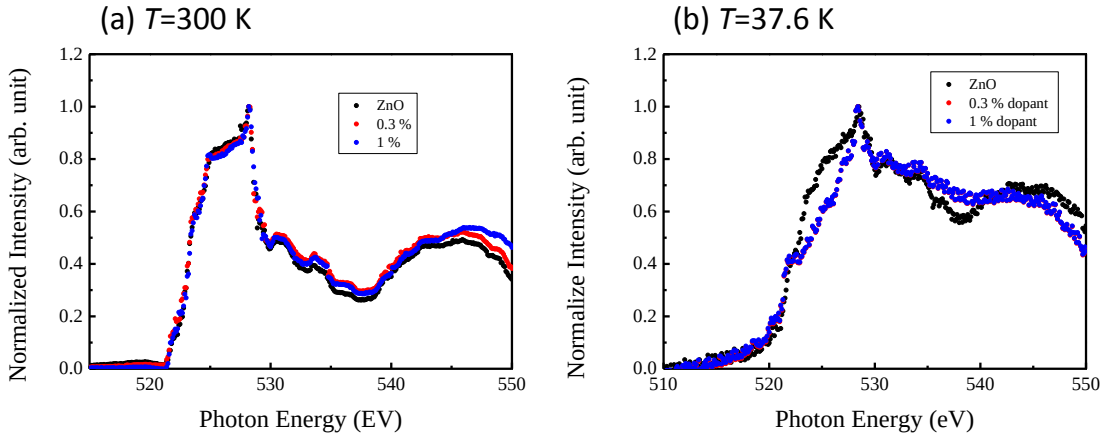

Figure 2. The spectra by X-ray absorption spectroscopy at (a)300 K and (b)37.6 K.. Three spectra means doping ration of Li. Red and blue solid points means Li doped sample at 0.3 and 1 %. Black solid points shows pure ZnO spectrum.

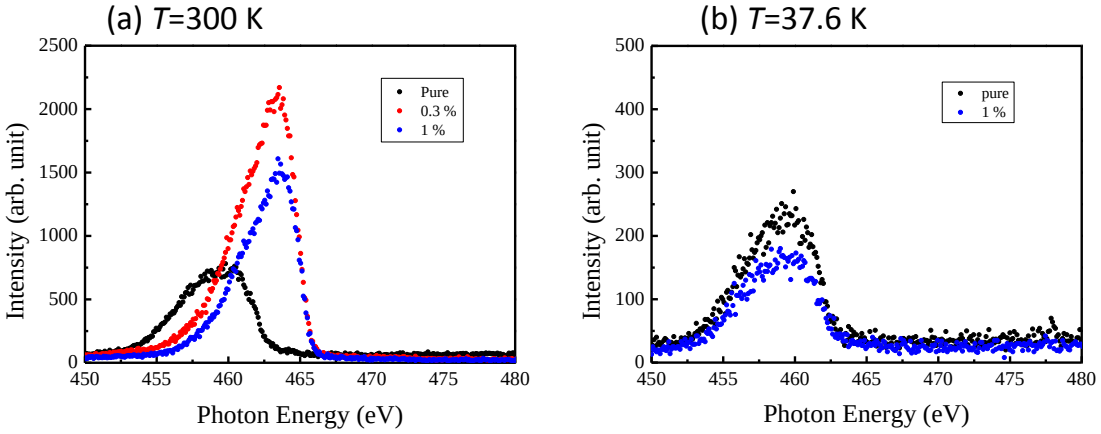

Figure 3. The spectra by X-ray emission spectroscopy at (a)300 K and (b)37.6 K.. Three spectra means dopant ration of Li. Red and blue solid points means Li doped sample at 0.3 and 1 %. Black solid points show pure ZnO spectrum.

previous report at 6% dopant.

The typical XAS spectra of all specimens were shown in Figure 2(a) 300 K and 2(b) 37.6 K. All XAS spectra have the bottom of conduction band at 521 eV and a maximum of absorption energy was 528 eV. The spectrum of doped specimens is very similar to pure specimen at 300 K. However, XAS spectra at 37.7 eV were shown small difference around 525, 538 and 550 eV. These differences might indicate ferroelectricproperty.

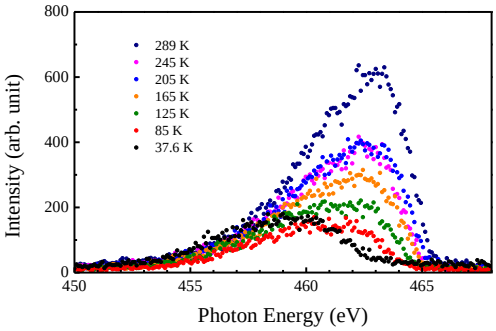

Figure. Temperatured dependence of XPS spectra of 1% doped ZnO. Each points shows the spectra every about 40 K from 289 K to 37.6 K.

The typical XES spectra were shown in Figure 3 (a) 300 K and 3(b) 37.6 K. From Figure 3(a), the impurity band was confirmed around 464 eV at 300 K in doped specimens. In low temperature phase, the impurity band is lost. Thus, temperature dependence of XES spectrum of 1 % doped specimen was measured every about 20 K. The temperature dependence of XES spectra was shown in Figure 4. The XES spectra were shown a decreasing of intensity around 464 eV accompanied with temperature. The behaviour is almost monotonic decreasing for temperature exclude between 220 K and 240 K. However, it is difficult to control temperature more precisely in this system. The spectra were shown the loss of impurity band.below 85 K. These behaviour might be indicate successive phase transition.

As a summary, XAS and XPS spectra were measured 1 and 0.3% Li doped ZnO and pure ZnO. XAS spectrum of Li doped ZnO is alomost same to pure ZnO at 300 K. However, distinction was appeared between doped ZnO and pure ZnO at low temperature. The XES spectra shows impurity band at room temperature by Li dopant. However, the impurity band was lost below 85 K. On the other hand, drastic temperature dependence was not observed at T_C.