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Preparation and characterization of $NaInO_2$ and $NaInS_2$

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$NaInO_2$ and $NaInS_2$ with α-$NaFeO_2$ layer type structure have been prepared and characterized by X-ray photoelectron spectroscopy to clarify the role of the anions in the electronic structures of the compounds. The In $3d_{5/2}$ binding energy for both compounds was the same, though the Na 1s binding energy of $NaInO_2$ was larger than that of $NaInS_2$ by 0.4 eV. The change in the Na Auger parameter, defined as the sum of Na 1s binding energy and KLL Auger kinetic energy, suggests that the difference in extra-atomic relaxation energy between the compounds causes the Na 1s binding energy shift. Discrete variational-Xα model cluster calculations for $NaInO_2$ and $NaInS_2$ mirrored the experimental valence band spectra and the difference of 0.5 eV in optical absorption energy of the compounds. The cluster calculation revealed that in $NaInO_2$ the highest occupied level is formed by an antibonding Na–O bond, whereas that in $NaInS_2$ is formed by a bonding Na–S bond. The covalent Na–S bond decreases the extra-atomic relaxation energy for Na 1s electron emission from $NaInS_2$.

Compounds of the general formula ABX_2 (A = alkali-metal ion, B = trivalent ion, X = O, S or Se) crystallizing in the α-$NaFeO_2$ layer type structure are of interest for the study of correlations between atomic interaction (chemical bonding) in solids and physical properties such as nonlinear optical susceptibility since A, B and X can be varied systematically in a given crystal structure, and the magnitude and sign of a physical property, absent for a free isolated atom, depends on the band structure of the solid. For α-$NaFeO_2$ type compounds the space group of the unit cell is D_{3d}^{5} ($R\bar{3}m$).[1] In the hexagonal system A, B and X occupy Wyckoff positions 3a, 3b and 6c, respectively.[2] Alternate layers of A and B atoms, separated by a layer of X atoms, appear every 0.5*c* in the *c*-axis direction. ABX_2 type compounds with identical A and B ions but different X ions are important in clarifying the correlations between the chemical bonds and the electronic structures of the materials. However, no report, as yet, available concerning the electronic structure of α-$NaFeO_2$ layer type compounds.

We studied $NaInO_2$ and $NaInS_2$ with α-$NaFeO_2$ structure since sulfides have a smaller electronegativity difference than oxides, and are expected to show more covalent electronic behavior than the ionic oxides. X-Ray photoelectron spectra and UV absorption spectra of the compounds revealed that the Na–S bond of $NaInS_2$ is more covalent than the Na–O bond of $NaInO_2$, and the energy difference between the filled valence and empty conduction bands of $NaInS_2$ is lower than that of $NaInO_2$. A first-principles molecular orbital (MO) cluster calculation for $NaInO_2$ and $NaInS_2$ by the discrete-variational (DV)-Xα method,[3] consistent with the electronic spectra, clarified the origin of the difference in the electronic properties of the compounds.

The XRD spectrum of $NaInO_2$ synthesized by calcination of an equimolar mixture of In_2O_3 and Na_2CO_3 for 1 h at 900 °C in air is shown in Fig. 1(a). The preparation of $NaInS_2$ films is described elsewhere in detail.[4] Initially, the Na–S layer was thermally evaporated from the Na_2S source on a Corning 7059 glass substrate, and then an In–S layer was deposited on the Na–S layer by reactive sputtering of the In_2S_3 target in H_2S gas. Upon annealing at 550 °C for 2 h in 5% H_2S–Ar, the bilayer precursor film crystallized to give the α-$NaFeO_2$ structure as revealed by the XRD trace in Fig. 1(b). The lattice constants *a* and *c* of the hexagonal cell of the $NaInO_2$ sample were 3.23_5 and 16.3_9 Å, respectively, while those of the $NaInS_2$ sample were 3.82_9 and 19.8_9 Å, respectively. These values are in close agreement with the reported values: $a = 3.235$ and $c = 16.35$ Å for $NaInO_2$,[5] and $a = 3.803$ and $c = 19.89$ for $NaInS_2$.[6]

A Surface Science Laboratories SSX-100 spectrometer with a monochromatized Al-Kα source was used for X-ray photoelectron spectroscopy at room temperature. The spectrometer

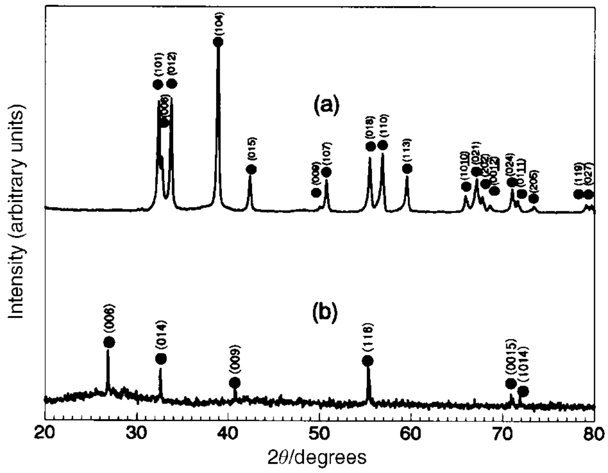

Fig. 1 X-Ray diffraction patterns of $NaInO_2$ (a) and $NaInS_2$ (b) measured by a Rigaku CN2013 diffractometer using Cu-Kα radiation. The samples were single phase and could be indexed with the α-$NaFeO_2$ structure.

Table 1 Core-level electron binding energy and Auger electron kinetic energy of $NaInO_2$ and $NaInS_2$ (eV)[a]

Electron	$NaInO_2$	$NaInS_2$
Na 1s	1071.5	1071.1
In $3d_{5/2}$	444.6	444.5
O 1s	531.4	—
S 2p	—	161.3
Na KLL	990.5	989.9
Na Auger parameter	2062.0	2060.9

[a] The estimated electron energy uncertainty is $\pm 0.1_5$ eV.

was calibrated utilizing Au $4f_{7/2}$ electrons (83.79 eV) with a full width at half maximum (FWHM) of 1.03 eV. Charging was referenced to C 1s electrons (285.0 eV).

In photoemission from solids, hole switching occurs in a time of $<10^{-16}$ s after photon absorption. In the delocalized screening process (10^{-13}–10^{-12} s) negative charge flows towards the photo-hole in order to immediately screen the created positive charge. A relaxation energy, R, lowering the observed binding energy, E_b, of the photoelectrons to below the orbital energy, $-\varepsilon$, of Koopmans' theorem is a consequence of this charge flow. The extra-atomic relaxation energy, R^{ex}, varies with changes in covalency of the chemical bonding. Core-electron binding energies reflect the effective charge and polarization effect *via* the orbital and extra-atomic relaxation energies.[7] E_b in the solid phase can be expressed as $E_b = -\varepsilon + R^{ex}$ where R^{ex} has a negative value.

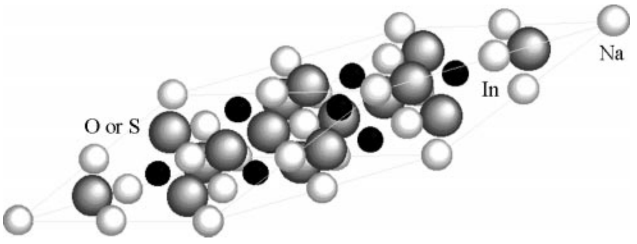

Fig. 2 $[Na_7In_6X_{38}]^{51-}$ (X=O or S) model cluster used for the calculation.

The Na 1s, In 3d, O 1s, S 2p and Na KLL electron energies of the samples are listed in Table 1. For both $NaInO_2$ and $NaInS_2$ the In $3d_{5/2}$ binding energies are the same, though the Na 1s binding and Na KLL kinetic energies of the $NaInO_2$ sample are higher by 0.4 eV than those of the $NaInS_2$ sample. The Na Auger parameter, defined as the sum of Na 1s binding energy and KLL Auger kinetic energy, is larger by 1.0 eV for $NaInO_2$ than for $NaInS_2$. The difference in the Auger parameter corresponds to twice the difference in extra-atomic relaxation energy of the photo-hole between the samples.[7] The decrease in the Na 1s electron binding energy (0.4 eV) corresponds to the extra-atomic relaxation energy (0.5 eV) for the Na 1s hole of the samples.

In solids with covalent bands or itinerant electron states, electrons can be readily transferred so as to screen the incremental positive charge (electronic relaxation). Such electronic relaxation cannot take place in ionic solids since there are no covalent bands. In ionic solids polarization of the electronic charge on neighboring ions is the only effective mechanism for screening of the photo-hole. If there were no differences in bonding and antibonding overlap populations between $NaInO_2$ and $NaInS_2$, the larger relaxation energy for Na in $NaInS_2$ compared with that for $NaInO_2$ could be rationalized by the greater polarizability of S^{2-} relative to O^{2-}. The larger relaxation energy for Na in $NaInS_2$ arises from the greater covalency of the Na–S bond in $NaInS_2$. As described below, the degree of Na mixing into the valence band orbitals of S in $NaInS_2$ is larger than that of O in $NaInO_2$, and the Na–S interaction in $NaInS_2$ is bonding whereas the Na–O interaction in $NaInO_2$ is antibonding. The covalent Na–S bond decreases the extra-atomic relaxation energy for Na1s electron emission from $NaInS_2$.

A first-principles MO calculation by the DV-Xα method employing the SCAT program code revealed that the larger polarization effect at Na in $NaInS_2$ relative to $NaInO_2$ arises from the more covalent Na–S bond in comparison to the Na–O bond at the highest level in the valence band. The electronic structure of a model cluster has been self-consistently

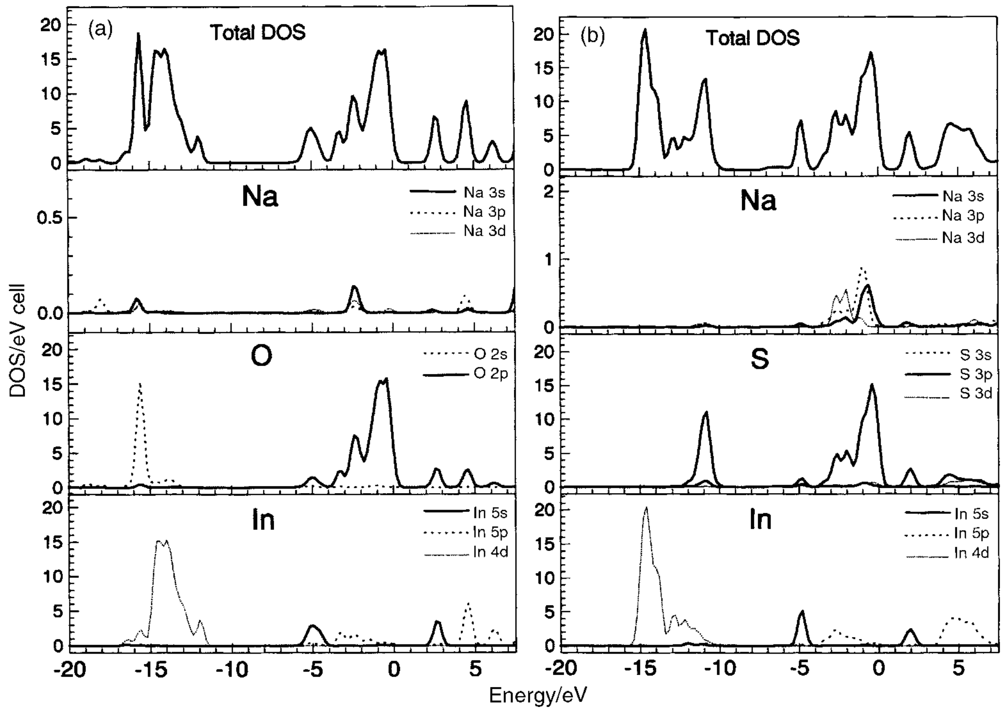

Fig. 3 Total density of states (TDOS) and partial DOS (PDOS) for $[Na_7In_6O_{38}]^{51-}$ (a) and $[Na_7In_6S_{38}]^{51-}$ (b) clusters. All of the DOS curves were constructed by broadening the discrete energy eigenvalues by Gaussian functions with 0.2 eV full width at half maximum.

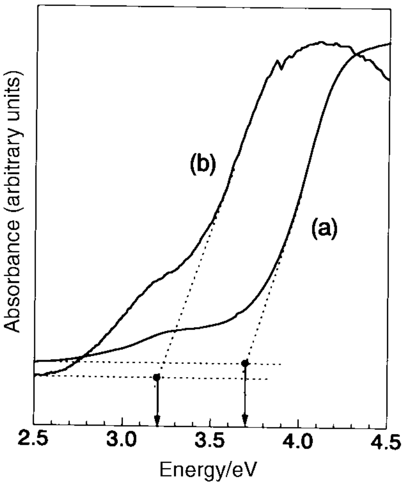

Fig. 4 UV–VIS diffuse reflectance spectra of $NaInO_2$ (a) and $NaInS_2$ (b) measured with a resolution of 0.002 eV using a JASCO V-550 spectrometer.

calculated using numerical atomic basis functions. A cluster model with 51 atoms $[Na_7In_6X_{38}]^{51-}$ (Na^+, In^{3+} and $X = O^{2-}$ or S^{2-}) shown in Fig. 2 was constructed on the basis of the crystal structure of α-$NaFeO_2$. The lattice parameters used were $a = 3.235$ and $c = 16.35$ Å for $NaInO_2$, and $a = 3.803$ and $c = 19.89$ Å for $NaInS_2$. The clusters was embedded in a Madelung potential generated by point charges outside the cluster.

Total density of states (TDOS) and partial DOS (PDOS) for $[Na_7In_6O_{38}]^{51-}$ and $[Na_7In_6S_{38}]^{51-}$ clusters are shown in Fig. 3(a) and (b). Energies are aligned so that the highest occupied MO (HOMO) is set to zero. The DOS with negative and positive energies denote occupied and unoccupied levels, respectively. The HOMO–LUMO energy splitting is 2.4 eV for $[Na_7In_6O_{38}]^{51-}$ and 1.7 eV for $[Na_7In_6S_{38}]^{51-}$. Substitution of S for O decreased the HOMO–LUMO splitting by 0.7 eV, which is consistent with the change of the experimental optical absorption energy of 0.5 eV as shown in Fig. 4.

The calculated DOS reproduced fairly well the valence band (VB) spectra of the samples as shown in Fig. 5. For the $[Na_7In_6O_{38}]^{51-}$ cluster, the upper valence band in the energy range −6.0 to 0 eV is mainly constructed from O 2p orbitals, and they strongly hybridize with In 5s and 5p orbitals. The band at 0 eV is primarily constructed from O 2p orbitals (with the contributions of In 5s and 5p orbitals being small). The lower conduction band from 2.0 to 5.0 eV is mainly constructed from In 5s and 5p orbitals. The presence of In 5s and 5p components in the O 2p band region indicates that the In–O bonding is not fully ionic but is partially covalent. However, mixing of the Na 3s, 3p and 3d orbitals with O 2s and 2p orbitals is essentially absent. The shape of the DOS function for the $[Na_7In_6S_{38}]^{51-}$ cluster showed differences relative to $[Na_7In_6O_{38}]^{51-}$. In particular, the S 3s and 3p orbitals show a degree of hybridization with the Na 3s, 3p, and 3d orbitals, as well as the In 5s and 5p orbitals. From these results, it is clear that $NaInS_2$ is more covalent than $NaInO_2$.

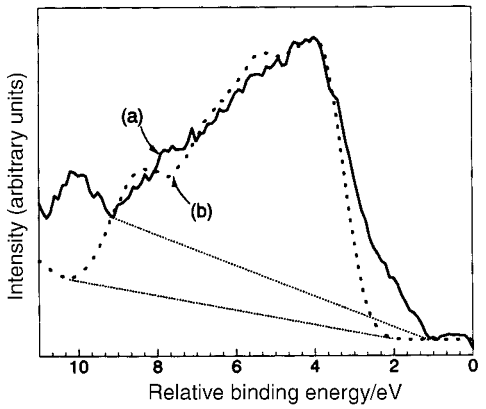

Fig. 5 Valence band spectra of $NaInO_2$ (a) and $NaInS_2$ (b) shown by solid and dotted lines, respectively. Thin broken lines indicate the linear background (BG) due to scattered secondary electrons in the solids.

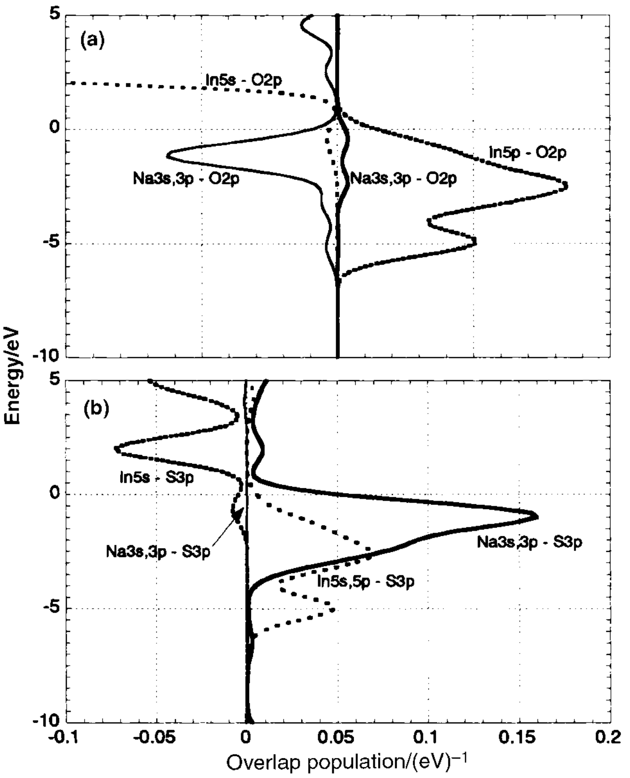

Fig. 6 Overlap-population diagrams of the $[Na_7In_6O_{38}]^{51-}$ (a) and $[Na_7In_6S_{38}]^{51-}$ (b) clusters.

Fig. 6(a) and (b) display the overlap-population diagrams of the $[Na_7In_6O_{38}]^{51-}$ and $[Na_7In_6S_{38}]^{51-}$ clusters indicating bonding (left) and anti-bonding contributions (right), respectively. For the $[Na_7In_6O_{38}]^{51-}$ cluster the In–O interaction shows a bonding contribution in the valence band and an antibonding contribution in the conduction band. The major part of the Na–O interaction shows an antibonding contribution in the valence band. On the other hand, for the $[Na_7In_6S_{38}]^{51-}$ cluster both In–S and Na–S interactions show a bonding contribution in the valence band region. It is readily understood that for $NaInS_2$ the extra-atomic relaxation energy at the Na site is smaller than for $NaInO_2$ since core-hole screening takes place more easily through the covalent Na–S bonding orbital in $NaInS_2$.

As expected from the smaller electronegativity difference between A, B and X in $NaInS_2$ relative to $NaInO_2$, we observe a smaller HOMO–LUMO splitting for $NaInS_2$ than for $NaInO_2$, both theoretically and experimentally, as shown in Fig. 3 and 4, which is consistent with the general trend of decreasing band gap energy upon reducing the electronegativity between cations and anions in ionic solids. A larger antibonding contribution of the Na–O bond in the $[Na_7In_6O_{38}]^{51-}$ cluster relative to the Na–S bond in the $[Na_7In_6S_{38}]^{51-}$ cluster should also be a consequence of the larger difference in electronegativity. In addition, a lower extra-atomic relaxation energy for Na in $NaInO_2$ relative to $NaInS_2$ as observed by X-ray photoemission is predicted.

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