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Hollandite-type compounds are showed with chemical formula as $A_xM_xM'_{8-x}O_{16}$. In A-site enter to alkali metal or an alkaline earth metal. In M-site enter to divalent or trivalent metal, and in M'-site enter to tetravalent metal ion. Metal-oxygen octahedron builds one-dimensional (1-D) tunnel taken along *c*-axis. The 1-D tunnel has cavity and bottle neck, and it is known that A-site will be settled in each cavity. In this study, the condition of guest ion sites of $K_{1.88}Ga_{1.88}Sn_{6.12}O_{16}$ was examined by single X-ray diffraction from 293K to 93K. And, the refinement used the following resiraint conditions; (a) full occupation at the metal site in a host structure, (b) charge neutrality in a whole crystal, (c) exist two K2-site (0, 0, z) shifted from cavity center <K1-site (0, 0, 0.5)> for one vacancy [1]. In refinement of $K_{1.88}Ga_{1.88}Sn_{6.12}O_{16}$ at 293K and 223K, the ADPs (Atomic Displacement Parameters) and the site occupation were optimized by using these restraint conditions. On the other hands, in refinement at 173K, 130K and 93K, the atomic coordinate of K1-site had to shift from cavity center for optimization. Furthermore, it was shown that the site occupation of K2-site increases from a theoretical value. Therefore, the newly following constraint conditions were introduced for optimizing refinement; (a') K2-site (0, 0, z) is the guest ion site which adjacent to vacancy, (b') the guest ion site next to K2-site is K3-site (0, 0, z'), and (c') other guest ion sites in cavity center are K1-site. By using these equations it was showed the degradation of ADPs and reliability factor of guest ion site. From these results, it was thought that two or more guest ion sites near vacancy would shift from cavity center.

Reference

[1] Y, Michiue, Acta.Cryst. B63 (2007) 577-583.

Keywords: hollandite, one-dimensional structures, guest ion

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New family of mixed nickel and group 13-14 metal tellurides with incommensurate structures

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Low-dimensional mixed nickel and main-group metal chalcogenides over the recent years have proven to be interesting both fundamentally and practically. Their structures, featuring extended systems of d-metal - p-metal bonds in a form of quasi-2D fragments separated by non-metallic ones, often provide unique physical properties (anisotropic conductivity, low-dimensional magnetism etc.). From a crystallographer's point of view, such compounds tend to present various problems associated with disorder and structural modulations. Here we present a new family of such compounds with the general formula $Ni_{1-x}MTe_2$ (M=Ga, In, Sn, Sb; x varies from 0 to 1, exact margins depend on M). All the compounds were obtained by a high-temperature (1023-1123K) synthesis from the elements and investigated by powder and single-crystal x-ray analysis, energy-dispersive x-ray spectroscopy and electronic microscopy. The structures of the compounds consist of the layers of heterometallic bonds, arranged according to the motif of the Ni_2In intermetallic structure, terminated by tellurium atoms that form the van der

Waals gap. The key feature of the structures is the presence of two partially occupied Ni positions: one in the heterometallic layer and the other in the van der Waals gap. The ordering of occupancies makes the structures incommensurate along the *c* axis and requires the introduction of the modulation vector. For different crystals, the *q*-vector varies between 0.26 and 0.32, which roughly corresponds to the quadruple or triple original subcell. The presence of the domains with different ordering in the crystals is also confirmed by the electronic microscopy. *This work was supported by RFBR (grant No.06-03-32789a) and Presidential Programme of Russian Academy of Sciences.*

Keywords: metal chalcogenides, nickel compounds, incommensurate structures

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Analysis of the misfit mixed-layer compound in the binary restacked nanosheet system $MnO_2-Ti_{0.91}O_2$

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A variety of layered compounds can be exfoliated into their unilamellar crystallites, namely nanosheets. Restacking of the nanosheets may provide a route to the fabrication of novel materials. The two-component colloidal nanosheets in the $MnO_2-Ti_{0.91}O_2$ system with various compositions were restacked by flocculation with alkali ions. X-ray powder diffraction patterns of the products show remarkable broadening reflections. The structures are suggested to be mixed-layer type of MnO_2 and $Ti_{0.91}O_2$. The powder pattern simulation process, prepared for analysis of layered composite crystals with one-directional disorder, based on the matrix method (Hendrics & Teller, 1942) was used. We considered (1) stacking disorder in restacked MnO_2 , (2) stacking disorder in restacked $Ti_{0.91}O_2$, and (3) sequence probabilities of MnO_2 and $Ti_{0.91}O_2$ nanosheets. Taking the chemical composition into consideration, three probability tables of (1), (2), (3) were unified into one large probability table. For 00zeta calculation, z coordinates of all atoms were used. As for hkzeta calculation except 00zeta, atom coordinates of MnO_2 were used on the trigonal MnO_2 cell and those of $Ti_{0.91}O_2$ were used on the orthorhombic $Ti_{0.91}O_2$ cell. Agreements in the total pattern fitting, between the experimental and calculated intensities, were satisfactory in all composition range. From the results, we can know the phase status, one-dimensional solid solution or one-dimensional phase separation, of the misfit mixed-layer material in the binary restacked nanosheet system of $MnO_2-Ti_{0.91}O_2$.

Keywords: diffuse diffraction, mixed layers, powder diffraction analysis

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Crystal structures and physical properties of donor type dithiolene complexes with cycloalkane rings

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Metal bis-dithiolene complexes have been intensively studied as conducting materials. Among them, acceptor type complexes provide various anion radical salts which exhibit superconducting and metallic behavior [1]. On the other hand, neither a metal nor a superconductor has been obtained from donor type complexes except for a salt of $[\text{Ni}(\text{dddt})_2]$ [2]. In this work, we examined modification of the dddt complex with terminal cycloalkane rings, and developed $[\text{Ni}(\text{Cn-dddt})_2]$ ($n = 3, 4, 5, 6$) to expand the materials chemistry of the donor type complexes. In the crystals of the neutral complexes, the cycloalkane rings exhibited various conformations which would affect physical properties in their cation radical salts. We succeeded in electrochemical crystallization of new cation radical salt $[\text{Ni}(\text{C3-dddt})_2]_3(\text{BF}_4)_2$. Other salts were also obtained by the similar procedures. We will discuss their electrical property based on the crystal structure.

[1] R. Kato, *Chem. Rev.*, 104 (2004) 5319.

[2] L. A. Kushch *et al.*, *J. Mater. Chem.*, 5 (1995) 1633.



Keywords: condensed matter, conducting materials, complexes

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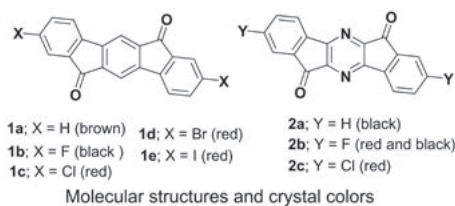
Crystal structures of indenofluorenediones and diindenopyrazinediones showing FET characteristics

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We have found indeno[1,2-b]fluorene-6,12-diones **1** and diindenopyrazinediones **2** are attractive n-type semiconductors for organic field-effect transistors (OFETs),¹⁾ whose crystal structures and colors are dependent on the halogen substituents introduced at the terminal positions. After sublimation of the crude product of **2a** with a pyrazine and no halogen groups, black crystals were obtained. On the other hand, in the case of compound **2b** with fluorine atoms, red crystals as well as black ones were obtained. We have succeeded in carrying out X-ray analyses of both single crystals and found the overlap patterns of the molecules are considerably different. In the red crystal only a half of the molecule is overlapped, whereas in the black crystal the whole molecule is involved in the overlap. The films of these derivatives deposited on SiO_2/Si substrates were investigated by X-ray diffraction in reflection mode (XRD). In the XRD measurement of **2b**, a clear difference depending on the crystal morphology was observed. We will discuss here about the relationship between the crystal structures and film morphologies.

(1) *Chem. Mater.* **2008**, in press.



Keywords: organic semiconductors, field-effect transistors,

polymorphism

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Genuine organic crystal exhibiting giant negative magnetoresistance

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A coexisting system of conductivity and magnetism consisting of a genuine organic material has become one of the current targets in the field of "molecular magnetism". Here we prepared a new type of the spin-polarized donor, BTBN, in which two bromine atoms are introduced at the dithiole ring to increase the intra- and inter-columnar interactions of donor units. The novel donor radical formed needle crystals of $(\text{BTBN})_8 \text{C}_6\text{H}_{14}$ with a size of ca. $0.1 \times 0.1 \times 5$ mm, including n-hexane in a channel structure. BTBN stacks along the c axis with the interplanar distance of 3.458(2) and 3.472(3) Å. The charge transfer band of the polycrystalline sample extended over to ca. 1400 cm^{-1} , suggesting a narrow gap between the valence and the conduction bands. This neutral crystal turns out to exhibit the negative magnetoresistance of -70 % at 5 K under 9 T. We found that the source drain current (IDS) of BTBN on a surface-oxidized silicon wafer increased by the application of both negative and positive gate voltage (VG). Moreover, the IDS values increased appreciably (ca. three times) when the external magnetic field of 5 T is applied at 2 K.

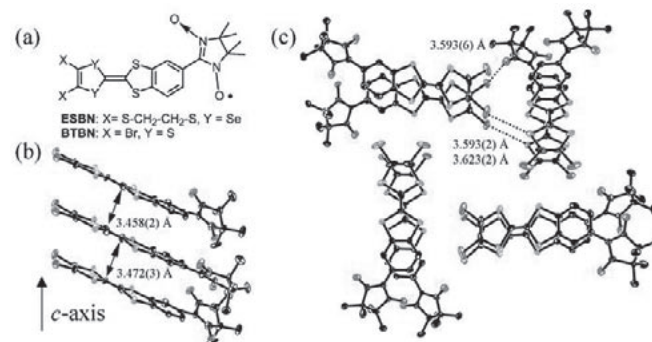


Fig. 1. Crystal structure of BTBN: Tetragonal, $P4_2/m$, $a = b = 33.327(4)$, $c = 7.617(1)$ Å, $Z = 16$
(a) Molecular structure of ESNB and BTBN (b) Stacking of BTBN along the c axis
(c) Arrangement of BTBN in the ab plane

Keywords: donor radical, negative magnetoresistance, field effect transistor

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Development of organic NLO materials for terahertz-wave generation

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