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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

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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 $Ni_{3-x}MTe_2$ (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.*

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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 unilameller 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-$Ti_{0.91}O_2$.

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

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