Intergrowth of Two Different Layered Networks in the Metallic Copper Oxyselenide $Na_{1.9}Cu_2Se_2{\cdot}Cu_2O$

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Solid-state oxy-chalcogenides of the late transition metals are rare. One reason for this may be the relative low oxophilicity and high chalcophilicity of these metals. An oxy-chalcogenide is defined as a compound with metal-oxide and metal-chalcogen bonds but no direct O-Q (Q = S, Te) bonds. Even though numerous copper chalcogenides[1] and copper oxides[2] exist, no mixed copper oxychalcogenides have been reported. Since these materials display interesting electronic properties (e.g., metallic and charge density wave properties in chalogenides[3] and high T_c superconductivity in oxides[4]), it is intriguing to consider the potential properties of mixed compounds. During our investigations of the reactivity of Cu with various polychalcogenide fluxes such as Na_2Se_x we isolated an unusual new compound $Na_{1.9}Cu_2Se_2{\cdot}Cu_2O$ (**I**) with unprecedented mixed Cu-Se/Cu-O features. This is the first layered oxyselenide and is composed of two alternating, independent Cu/Se and Cu/O frameworks. We report here the synthesis, structure, and charge-transport properties of this new material.

$Na_{1.9}Cu_2Se_2{\cdot}Cu_2O$ was discovered during our investigations of the reactivity of Cu in a Na_2Se_x flux. Unlike the K_2Se_x flux which tends to form Cu-polychalcogenides at 250-300 °C, Na_2Se_x requires a slightly higher melting temperature and does not tend to form polychalcogenide compounds.[5] Instead, two competing phases containing monoselenides, $Na_3Cu_4Se_4$[6] and $Na_{1.9}Cu_2Se_2{\cdot}Cu_2O$, were isolated. Given that copper is one of the most chalcogenophilic elements, particularly in its +1 oxidation state, and that under Se_x^{2-} flux conditions the concentration of various Se_x^{2-} ions is very high, the isolation of an oxygen containing phase is quite surprising. At this stage we suspect that an impurity in Na_2Se_x is likely the oxygen source in the reaction.[7] Use of exceedingly pure sodium to prepare Na_2Se_x yielded primarily $Na_3Cu_4Se_4$ with $Na_2Cu_2Se_2{\cdot}Cu_2O$ still being present in small amounts. The yield of $Na_2Cu_2Se_2{\cdot}Cu_2O$ was maximized using Cu_2O as starting material, instead of Cu, in the ratio of $Cu_2O/Na_2Se_{3.6}$ of 1:3 at 340 °C.[8] These conditions yielded large (1 mm) single crystals, but small needles of $Na_3Cu_4Se_4$ were still evident as a minor (<5%) phase. When the reaction temperature was increased to 450 °C, the amount of $Na_{1.9}Cu_2Se_2{\cdot}Cu_2O$ increased.

The intriguing structure of $Na_{1.9}Cu_2Se_2{\cdot}Cu_2O$ features two independent but isoperiodic layers of $[CuSe]_n^{n-}$ and $[Cu_2O]$ as shown in Figure 1.[9] The compound can be considered as a perfect 1:1 intergrowth of layers of NaCuSe[10] and layers of Cu_2O. Figure 2 shows views of the two individual layers. The $[CuSe]_n^{n-}$ in the NaCuSe fragment is an anti PbO-type layer, where Cu (on $\bar{4}m2$ site) has tetrahedral geometry and Se (on 4*mm* site) has square-pyramidal geometry. Isolated NaCuSe exists and has the same structure as that found in **I**.[10] The average Cu-Se bond distance of 2.484 (3) Å in **I** is slightly smaller than that found in NaCuSe (2.55 Å).

The Cu_2O layer represents a new structural type. In this layer, Cu is linearly coordinated and is situated on a crystallographic mmm site while oxygen occupies a 4/*mmm* site and adopts a remarkable square-planar geometry. Thus, the Cu_2O layer can be considered as an anti CuO_2-type layer, commonly found in high-T_c cuprate superconductors.[11] The average Cu-O bond distance is 1.957 (1) Å, in the normal range found in known Cu/O compounds

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(5) Kanatzidis, M. G.; Park, Y., to be published.

(6) Kanatzidis, M. G.; Park, Y., submitted for publication.

(7) This may be due to surface oxidation of the starting sodium metal (producing NaOH) used during the preparation of Na_2Se_x.

(8) 0.187 g (1.5 mmol) of Na_2Se, 0.034 g (0.50 mmol) of Cu powder and 0.316 g (4.0 mmol) of Se powder were mixed together and loaded in a Pyrex tube which was flame-sealed under vacuum (~10^{-3} Torr). The tube was placed in a computer-controlled furnace and heated at 340 °C for 96 h and slowly cooled to 50 °C at a rate of 2 °C/h. The black, thin plate crystals were obtained by removing excess sodium polyselenides with DMF under an N_2 atmosphere (yield 76% based on the Cu used). The product was ofen contaminated with a competing phase, $Na_3Cu_4Se_4$. Since the product contains oxygen, we have also used Cu_2O instead of Cu metal. 0.187 g (1.5 mmol) of Na_2Se, 0.143 g (1.0 mmol) of Cu_2O powder, and 0.316 g (4.0 mmol) of Se powder were mixed and loaded in a Pyrex tube which was flame-sealed under vacuum (~10^{-3} Torr). The tube was placed in a computer-controlled furnance and heated at 330 °C for 7 days and cooled slowly to 50 °C at a rate of 2 °C/h. Black, thin plate crystals were obtained by removing excess sodium polyselenides with DMF under an N_2 atmosphere (yield 84% based on the Cu used). The product was also contaminated with a small amount of thin needles (2 μm × 20 μm) of $Na_3Cu_4Se_4$.

(9) $Na_{1.9}Cu_2Se_2{\cdot}Cu_2O$: fw 474.08, space group *I*4/*mmm*, *a* (Å) = 3.914 (2), *c* (Å) = 21.623 (4), *V* (Å^3) = 331.3 (4), *Z* = 2, at 23 °C. Crystal size (mm) 0.03 × 0.16 × 0.18. Radiation Mo Kα, μ (Mo Kα, cm^{-1}) 236.2. D_{calc} (g/cm^3) 4.75. $2\theta_{max}$ (deg) 55. Scan method $\omega/2\theta$. No. of data collected 254. No. of unique data 151. No. of data used 107 ($F_o^2 > 3\sigma(F_o^2)$). No. of atoms 5. No. of variables 13. The structure was solved with direct methods. Final R/R_w 5.3/7.7. Empirical absorption corrections based on ψ-scans and DIFABS were applied. There is only one crystallographically distinct Na atom situated on a crystallographic 4*mm* site. The Na atoms interact ionically only with Se atoms at 3.070 (9) Å and have a square-pyramidal geometry.

(10) Savelsberg, G.; Schäfer, H. *Z. Naturforsch.* **1978**, *33B*, 370-373.

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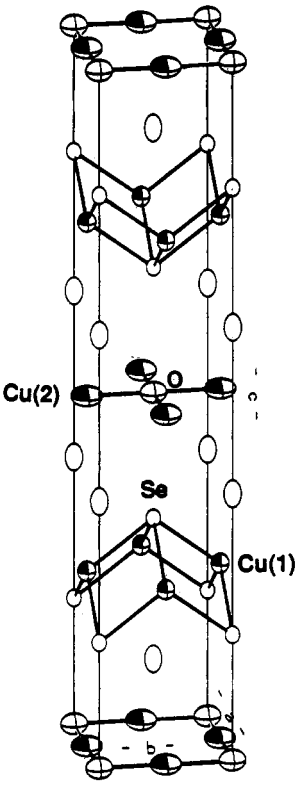

Figure 1. Unit cell of $Na_{1.9}Cu_2Se_2{\cdot}Cu_2O$ with atom labeling.

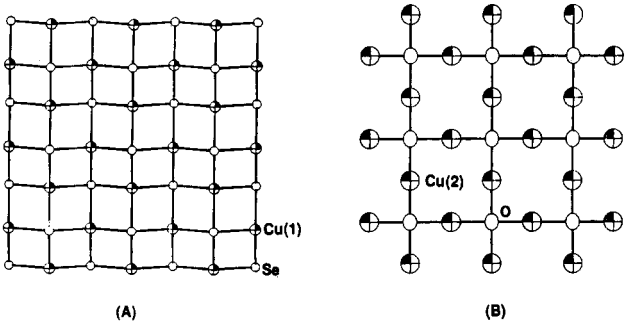

Figure 2. Views of the separate $[CuSe]_n^{n-}$ and $[Cu_2O]$ layers in $Na_{1.9}Cu_2Se_2{\cdot}Cu_2O$.

(1.85–1.98 Å). There are short Cu- -Cu contacts in the layers in the range of 2.768 (2) Å, but no Cu- -Cu contacts between the layers. The square-planar geometry of oxygen is the most unusual feature of I and is rare in metal oxide chemistry. One known example is found in NbO,[12] which contains square-planar Nb and O atoms. The stabilization of square-planar oxygen is surprising and at this stage we cannot offer a satisfactory explanation for its origin. Nevertheless, whether it is due to efficient packing of the layers or to electronic reasons, this suggests that such square-planar geometry may be more common than previously thought and may be adopted at defect sites in more conventional oxides as well as high T_c superconductors. The structure of bulk Cu_2O involves two interpenetrating *tetrahedral* Cu_2O frameworks, each isostructural to SiO_2. The oxygen in this compound is tetrahedrally surrounded by linear Cu centers.

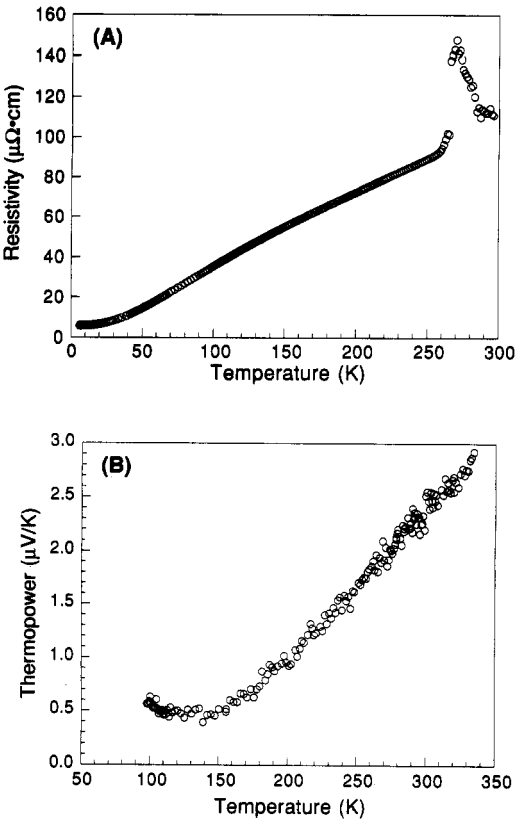

Figure 3. (A) Four-probe electrical resistivity of $Na_{1.9}Cu_2Se_2{\cdot}Cu_2O$ single crystals. The jump in the resistivity around 270 K is due to partial hydrolysis of Na^+ ions caused from the melting of water vapor condensed during the period of measurement. The measurement started at 5 K and the data were collected by increasing the temperature. (B) Thermolectric data as a function of temperature of $Na_{1.9}Cu_2Se_2{\cdot}Cu_2O$ single crystals showing p-type metallic behavior. Since the sample was under rough vacuum during the measurement the Na^+/H_2O reaction observed in the resistivity plots is not observed here. The thermoelectric power contributions of the gold contacting wires have been remove from the data.

In our initial crystal structure analysis we characterized this compound as $Na_2Cu_2Se_2{\cdot}Cu_2O$. This formula suggests an electron precise material which is expected to exhibit a bandgap and thus be a semiconductor. However, a study of its electrical properties revealed that I is actually a metal (see below). This unexpected property prompted us to reexamine the composition of the compound for nonstoichiometry by careful refinement of the occupancies of all atoms in the unit cell. The best fit was obtained by introducing a slight Na^+ deficiency, which quickly converged to the formula $Na_{1.9}Cu_2Se_2{\cdot}Cu_2O$.[13] This partial removal of Na^+ from the lattice is accompanied with the creation of electron vacancies (holes) in the framework (i.e., oxidation), resulting in a partially empty valence band.

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(12) *Structural Inorganic Chemistry*; Wells, A. F., Ed.; Oxford University Press: New York, 1987; p 538.

(13) (a) Refinement of the structure as $Na_2Cu_2Se_2{\cdot}Cu_2O$ gave R/R_w of 5.5/7.8‰ and an isotropic temperature factor for Na of 3.23. At $Na_{1.9}Cu_2Se_2{\cdot}Cu_2O$ the temperature factor of the Na atom was 2.89. Occupancy refinement of all the Cu, Se, and O sites (with a constant scale factor) resulted in R/R_w values of 9/11% or higher, and thus we concluded that nonstoichiometry on those sites is less likely. On the basis of the Hamilton significance test,[13b] the drop in R values obtained upon changing the occupancy of the Na atom from 2 to 1.9 is only significant to a 90% confidence level. Thus, the results presented here are only the ones that best fit the currently available experimental data. We recognize that other defects, superstructures in the two sublattices and nonstoichiometry in other atoms in the lattice may still be there. The final e density in the difference e density map was found at extremely low levels at coordinates −0.169–0.487, 0.00 of 2.85 e/Å^3 and at 0.00, 0.00, 0.208 of 2.22 e/Å^3. (b) Hamilton W. C. *Acta Crystallogr.* **1965**, *18*, 502–510.

On the basis of $Na_{1.9}Cu_2Se_2 \cdot Cu_2O$, one would expect p-type metallic behavior.

The charge-transport measurements on single crystals of $Na_{1.9}Cu_2Se_2 \cdot Cu_2O$ along the (001) plane show that the resistivity decreases linearly with falling temperature and levels off to a constant value (so called residual resistivity) below 20 K. The resistivity increases from 5×10^{-6} Ω cm at 5 K to 1.1×10^{-4} Ω cm at room temperature. This metallic behavior is shown in Figure 3. The temperature dependence of the thermoelectric power (Seebeck coefficient) shows a very small positive value of 0.5–3 μV/K in the temperature range of 100~330 K as shown in Figure 3. The small and linearly increasing Seebeck coefficient with rising temperature confirms the p-type character.

An interesting issue is hole delocalization: Do the holes delocalize in the $[CuSe]_n^{n-}$ or the Cu_2O layers? Assuming that the Se sites are the most electron-rich locations in the lattice, we would expect the holes to delocalize on a Se based p-band. This is consistent with the shorter Cu–Se distances in I compared to those in NaCuSe. In a less likely case, the square-planar oxygen geometry may also represent an electron rich site from which electrons could be removed. Careful X-ray photoelectron spectroscopic studies coupled with band structure calculations may be needed to successfully address this question.

$Na_{1.9}Cu_2Se_2 \cdot Cu_2O$ is the first example of cocrystallization of a copper–oxide and copper–chalcogenide framework. The fortuitous perfect epitaxial relationship of the two layers may be the driving force for the stabilization of this compound.[14] Its formation from Cu_2O as starting material teaches us a potential new synthetic strategy for obtaining new oxychalcogenides in which metal oxides can be used in reactions with polychalcogenide fluxes. $Na_{1.9}Cu_2Se_2 \cdot Cu_2O$ may be the first member of a large family of $(Na_{1.9}Cu_2Se_2)_n(Cu_2O)_m$ materials with alternating blocks of NaCuSe and Cu_2O layers.

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Supplementary Material Available: Tables of crystal structure analysis, atomic coordinates of all atoms, anisotropic and isotropic thermal parameters of all non-hydrogen atoms (6 pages); listings of calculated and observed ($10F_o/10F_c$) structure factors for $Na_{1.9}Cu_2Se_2 \cdot Cu_2O$ (1 pages). Ordering information is given on any current masthead page.

(14) Another interesting example of two independent but commensurate sublattices is found in the $(AMnX)_2(MnO_2)$ (A = Sr, Ba; X = P, As, Bi) family of compounds. (a) Brechtel, E.; Cordier, G.; Schafer H. *Z. Naturforsch.* **1979**, *34B*, 777. (b) Stetson, N. T.; Kauzlarich, S. M. *Inorg. Chem.* **1991**, *30*, 3969–3971.