can correspond to the unique intermolecular, intra unit cell vibration sought in this treatment. These two bands correspond to the monomer. None of the other Raman frequencies observed correspond to a reasonable integer unit above the monomer, thus ruling out structure C. This finding corroborates the Mössbauer IS and QS data which specify four-coordination at tin, ruling out structure B, and the magnitude of the slope of the plot of area vs. temperature also rules out a polymeric lattice as in structure C. Thus we are forced to conclude that the triphenyltin dithiophosphate esters adopt a rare, monomeric, monodentate structure such as A.[44]

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Preparation and Properties of a Copper Niobium Oxyfluoride

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A fluorinated phase of copper niobium oxide with the formula $CuNb_2O_{5.3}F_{0.7}$ has been synthesized. The oxyfluoride powder pattern can be indexed on the basis of orthorhombic symmetry with $a = 9.665$ (5), $b = 10.395$ (3), and $c = 7.847$ (3) Å. Magnetic susceptibility data indicate a Curie–Weiss behavior consistent with the quantity of Cu^{2+} (d^9) present. The measured room-temperature resistivity is 0.5 Ω cm, and the electronic activation energy of 0.06 eV indicates some electron delocalization.

Introduction

The chemistry of transition metal oxyfluorides has aroused interest in recent years. In view of the fact that oxygen and fluorine have similar ionic radii[1] the possibility of fluoride incorporation into these systems exists without creation of large structural changes. Such substitutions have been shown to occur in the formation of spinel,[2] magnetoplumbite, garnet,[3] perovskite,[4] and rutile[5] oxyfluorides.

Another group of compounds with rutile related structures are formed when niobium pentoxide reacts with divalent and trivalent ions. In nature the mineral columbite, iron(II) or manganese(II) niobate, occurs with a unique structure. The objective of this work was to prepare and characterize a copper niobium oxyfluoride crystallizing with the columbite structure. The preparation was achieved by a new fluorination technique.

Experimental Section

Material Preparation. The starting material, $CuNb_2O_6$, was prepared by solid-state reaction between CuO, which was synthesized by successive oxidation of metallic copper (Johnson Matthey) under oxygen atmosphere, and Nb_2O_5 (Kawecki Berylco Industries, Inc.). The proper molar ratio of the two oxides was mixed in a high-speed mill and pressed into small pellets. The pellets were then placed on a platinum disk and heated at 1000 °C in a tube furnace for 24 h under a continuous flow of oxygen. The material was obtained as a dark green powder.

Fluorination. The fluorination apparatus[6] consisted of two nickel tubes placed in two separate tube furnaces. HF was generated by means of the thermal decomposition of potassium bifluoride (Research Organic/Inorganic Chemical Corp.), a sufficient quantity of which was placed in a nickel boat and positioned in one of the nickel tubes. The sample was then placed on platinum in a second nickel boat and positioned in the second nickel tube. The two tubes were connected together and also to the carrier gas tanks in such a fashion that as the HF was generated, it was carried by a gas stream which first passed through a flowmeter and a phosphorus pentoxide drying tube and then over the sample and finally exited into a trap containing a 5% solution of sodium hydroxide.

The fluorination reactions were carried out on pressed pellets of copper niobate by using 15% H_2/Ar as the carrier gas which also served as reducing agent. The apparatus described above allowed working temperatures of up to 800 °C. The fluorinations were usually allowed to take place for 4 h. At 800 °C dark brown, well-sintered disks were produced which were then subjected to chemical and physical as well as X-ray measurements.

X-ray Analysis. The X-ray diffraction data were collected on a powder sample by using a Guinier camera with copper Kα radiation ($\lambda = 1.5405$ Å) and silicon ($a = 5.43062$ Å) as an internal standard.

Chemical Analysis. The fluoride content of the sample was leached out by means of sodium hydroxide fusion in a platinum boat. The process was carried out in a closed system to ensure that no fluoride escaped. The fluoride ion concentration was then determined by using a fluorine-sensitive electrode (Orion 94-09) and a Leeds and Northrup 7415 pH meter.

Density Measurements. Density measurements were made by using a hydrostatic technique on Archimedes principle.[7] The liquid medium was perfluoro-1-methyldecaline (Pierce Chemical Co.), and the balance

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Table I. X-ray Data on $CuNb_2O_{5.3}F_{0.7}$

intens	d_{obsd}, Å	d_{calcd}, Å	hkl
6	5.209	5.198	020
1	4.869	4.833	200
90	3.932	3.923	002
3	3.467	3.465	030
100	3.140	3.131	022
50	3.079	3.077	310
1	2.871	2.865	311
3	2.727	2.738	320
3	2.599	2.599	040
53	2.451	2.453	113
26	2.422	2.421	312
5	2.411	2.416	400
2	2.354	2.353	410
2	2.313	2.309	401
2	2.167	2.167	042
5	2.114	2.114	142
80	2.088	2.088	033
3	2.032	2.032	150
8	2.008	2.009	051
3	1.975	1.977	242
30	1.960	1.962	004
5	1.860	1.856	251
5	1.843	1.844	043
20	1.828	1.833	024
31	1.807	1.805	152
28	1.789	1.790	214
2	1.764	1.765	521
2	1.733	1.732	060
2	1.706	1.705	160
30	1.665	1.666	161
17	1.655	1.654	314

used was a Mettler H-54. The liquid medium was standardized by using a high-purity silicon standard (Atomergic Chem. Metals), ρ = 2.328 g/cm^3.

Magnetic Measurements. Magnetic susceptibilities were measured by using a Faraday balance[8] over the range from liquid nitrogen to room temperature at a field strength of 10.4 kOe. Honda–Owen plots were also made in order to determine the presence or absence of ferromagnetic impurities. The data were then corrected for core diamagnetism.[9]

Electrical Measurements. Electrical measurements were made by using the standard van der Pauw technique.[10] Indium leads were placed on the sample ultrasonically and then soldered to the terminals of high-resistivity epoxy cement blocks.

Results and Discussion

Fluorination of $CuNb_2O_6$ resulted in the formation of an oxyfluoride with a density of 5.18 ± 0.1 g/cm^3. The X-ray diffraction data for this compound are given in Table I. The peaks were tentatively indexed on the basis of an orthorhombic unit cell with the cell parameters a = 9.665 (5), b = 10.395 (3), and c = 7.847 (3) Å. However, the relative intensities and positions of a few of these peaks led to some reservation with respect to the assignment made; the unit cell may be of lower symmetry.

The results of the chemical analysis indicated the presence of 0.7 mol of fluorine/1 mol of the oxyfluoride. Moreover, the magnetic data indicated that the material is paramagnetic containing no ferromagnetic impurities as determined by the field independent Honda–Owen plot. Figure 1 shows the plot of χ^{-1} vs. temperature for copper niobate, $CuNb_2O_6$, with a μ_{eff} of 2.08 μ_B. This value is within the expected range of magnetic moments of 1.8–2.2 μ_B[8] observed for Cu^{2+} (d^9) systems.

Figure 2 affords the plot of χ^{-1} vs. temperature for the oxyfluoride system with an apparent moment of 0.68 μ_B. This
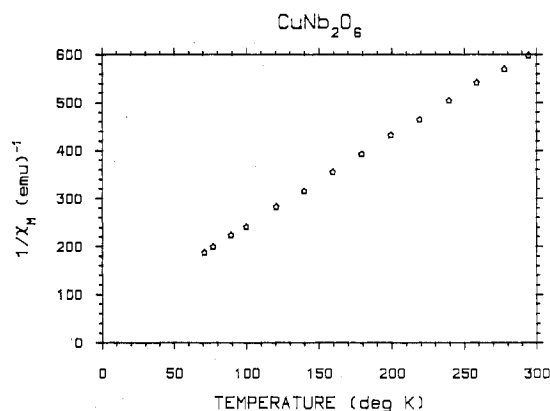

Figure 1. Thermal variation of the molar magnetic susceptibility of copper niobate. The slope corresponds to a μ_{eff} of 2.08 μ_B.
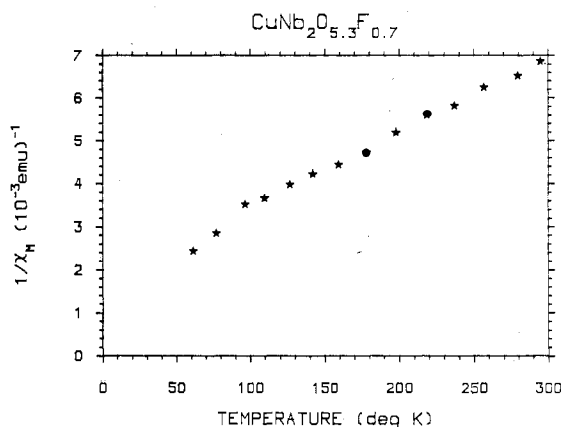

Figure 2. Thermal variation of the molar magnetic susceptibility of fluorinated copper niobate. The slope corresponds to a μ_{eff} of 0.68 μ_B.
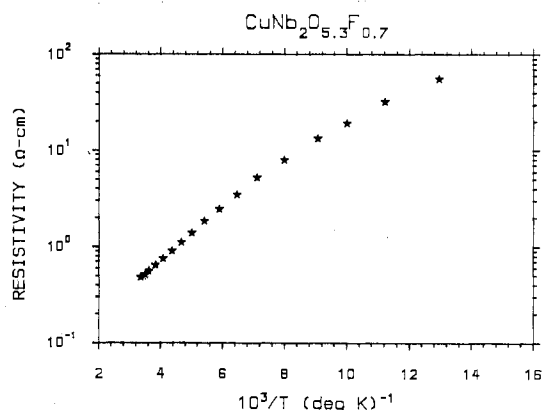

Figure 3. Thermal variation of the resistivity of fluorinated copper niobate. The slope corresponds to an activation energy of 0.06 eV.

value corresponds to the presence of 0.32 mol of Cu^{2+} in the fluorinated sample with the remainder being Cu^+. This is in agreement with the value of 0.3 mol of Cu^{2+} obtained from chemical analysis.

The resistivity measurements are given in Figure 3. The material shows a room-temperature resistivity of 0.5 Ω cm and a low activation energy of 0.06 eV. As observed for other conducting transition metal compounds,[11,12] the failure to obtain a Hall voltage indicates low mobility (<0.1 cm^2/V) and a large number of carriers ($>10^{18}$).

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Attempts were made to prepare copper niobium oxyfluorides with varying amounts of fluorine. The two procedures in the fluorination of $CuNb_2O_6$ involved either the use of H_2/Ar as the carrier gas or the use of pure hydrogen. The former method gave essentially identical products between 600 and 800 °C. Fluorination did not occur below 600 °C. The latter procedure tended to result in the formation of decomposition products.

In view of these observations, it can be concluded that the limit of fluorination was reached and that the maximum amount of fluorination achieved corresponded to the compound $CuNb_2O_{5.3}F_{0.7}$. Moreover, the high electrical conductivity of this compound may be attributed to some delocalization of the 3d electrons probably via metal–oxygen–metal overlap. It is of interest to note that such delocalization occurs despite the presence of fluoride ions which favor localization of 3d electrons.

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Synthesis of Copper Thioxo- and Dithioimidodiphosphinates. Infrared and Raman Spectra of Imidodiphosphinates

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Syntheses of several tetraphenyldithioimidodiphosphinate (L) copper complexes, $[Cu^I_4L_3^+][Cu^ICl_2]CCl_4$, $[Cu^I_4L_3^+][ClO_4^-]$, $Cu^I_3L_3$, $Cu^I_3L_3 \cdot 2^1/_2CCl_4$, Cu_3L_4, and $[Cu^{II}(NH_3)_4^{2+}][L^-]_2$, and tetraphenylthioxoimidodiphosphinate (L′) complexes, $Cu^{II}L'_2$ and $Ni^{II}L'_2$, are described. Electronic absorption and EPR spectra of $Cu^{II}L'_2$ and electronic spectra of $Ni^{II}L'_2$ indicated a square-planar MO_2S_2 core geometry for these chelates. Oxidation of L-containing cuprous complexes and redox activity of $Cu(II)$–L combinations yielded the oxidized ligand, HL′. Infrared and Raman spectra of the above copper chelates as well as HL, NaL, $Mn^{II}L_2$, $Fe^{II}L_2$, and $Co^{II}L_2$ were measured between 1700 and 200 cm^{-1}. The resonance Raman spectrum of $Cu^{II}L_2$ was obtained and compared with similar spectra of Cu_3L_4. The infrared spectra of tetramethyldithioimidodiphosphinates (L″), HL″ and $Co^{II}L''_2$, and the Raman spectrum of HL″ were also measured. Vibrational mode assignments of $\nu(PN)$, $\nu(PO)$, $\nu(PC)$, and $\nu(MS)$ and phenyl and methyl group bands are made. Structural and bonding changes are correlated with these vibrational frequencies.

Introduction

Ligands that are identified by the generic name imidodiphosphinate, $(R_2XPNPYR_2)^-$, where $R = CH_3$ or C_6H_5 and $X,Y = S$, O, or NH, were first synthesized by Schmidpeter et al.[1] Structure and bonding in dithioimidodiphosphinate (L) ligands make them unique among sulfur donors in several respects: (1) stereochemical trends in $M^{II}L_2$ complexes, M = first-row transition metal; (2) redox behavior of metal and ligand in complex formation; and (3) nonrigidity of chelate ring geometry.

The tetrahedral geometry about P atoms of L was expected to produce appropriate puckering of six-membered chelate rings in $M^{II}L_2$ complexes and so, possibly, induce tetrahedral geometry about the central metal atom. Tetrahedral $M^{II}S_4$ core structures[2] were verified for Mn(II), Fe(II), Co(II), and, surprisingly, Ni(II) and Cu(II) as well. The latter two metal ions generally form square-planar complexes[3] with sulfur ligands. Analyses of d–d bands in the electronic spectra[2a,d] of $M^{II}L_2$ compounds did not indicate an unusually low ligand field strength for this ligand. Nor did magnetic and electronic

spectral evidence for planar Ni(II) and Cu(II) complexes[2a,4] with imidodiphosphinates, X = O, Y = O, and X = NH, Y = NH, show that tetrahedral geometry was a common characteristic for all imidodiphosphinates. Since explanations for the observed trend for dithioimidodiphosphinates have not been put forward, we explored the tendency of analogous $M^{II}S_2O_2$ core complexes to form similar tetrahedral structures.

Metal ion–dithioimidodiphosphinate solution redox properties also deviate from the norm for sulfur donor ligands. Stable $Mn^{II}L_2$, $Fe^{II}L_2$, and $Co^{II}L_2$ compounds were isolated[2] in aqueous solution and were immune to the usual air O_2-mediated oxidation of metal and/or ligand. On the other hand, cupric ion–L⁻ solutions were unstable.[2] Reduction of Cu(II) to Cu(I) and subsequent formation of cuprous complexes under ambient conditions were consistent with a characteristic feature of cupric ion–sulfur ligand systems. Preliminary reports[5] of multinuclear complexes of L with Cu(I) indicated no formation of dimeric disulfides[6] or thioethers[7] that were observed in the oxidation of some thiolate ligands. Details of the syntheses

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