05.224 CRYSTAL AND ELECTRONIC STRUCTURE OF $\{(\mu^2-\Pi)\}_3$(C03)50yBD0. By T. E. Hsu, D.-Y. Jan and S. C. Shen. Department of Chemistry, Ohio State University, Columbus, Ohio 43210, U.S.A.

The title compound (I) has been prepared and characterized by single-crystal X-ray diffraction as well as spectroscopic methods ($\mu_{C}, \mu_{B}, \mu_{N}$). The compound is a carbonyl boridyne capped O$_3$ triangle as shown in the figure.

The electronic structure of I has also been studied by using the Frenkel-Hall quantum chemical approach with a fragment analysis in terms of the metal cluster H$_3$(CO)$_9$O$_3$ capped ligand BOD. The calculation suggests that the spin-1/2 boron is electron rich and the $\pi$ system acts as an electron donor and electron acceptor. A localized MO description with a $\pi$-hybridized boron forms a divalent bond to the metal triangle and the remaining $\pi$ orbitals form multicentered $\sigma$ bonds to the O$_3$ cluster.

The BOC unit in I has $\beta$.C.(135)1 and C-OM.1451, while in H$_3$BOD (II) has B-OM.141 and C-OM.131. The CO stretching frequency is 2110 cm$^{-1}$ in I and 2120 cm$^{-1}$ in II. To explain this difference, nonparameterized Frenkel-Hall molecular orbital calculations are carried out on both I and II with a fragment analysis in terms of H$_3$(CO)$_9$O$_3$ and CO for the former, H$_3$B and CO for the latter. The calculation suggests that the back $\sigma$ bonding in I is more significant, due to the predominant movement of the electron density of the main O$_3$B bonding orbitals to the CO $\pi$ anti-bonding orbitals.

05.225 THE EFFECT OF CRYSTAL STRUCTURE AND PHASE STABILITY ON THE SUPERCONDUCTIVITY OF EQUATORIAL TERNARY PHILOID COMPOUNDS. By C. F. Weimer, Los Alamos National Laboratory, MST-5, Los Alamos, NM 87545, USA.

The equatorial ternary compounds MX$_3$ with M = Ti, Zr, or Hf, N = Ru or Os, and X = P or As typically crystallize at high temperatures in the ZrRuSi-type hexagonal structure (P6$_3$m, $\text{M}$ in $\text{M}$, and $\text{X}$ in $\text{X}$), and exhibit superconductivity at temperatures as high as 13.3 K for ZrRu (Barb, Ku, Weimer, Pisk, and Mattias, Proc. Natl. Acad. Sci. USA (1980) 77, 3132; Meisner, Ku, and Barb, Mater. Res. Bull. (1983) 18, 983). These compounds are metastable and crystallize at low temperature in the TiNiSi-type or TiFeSi-type orthorhombic structures. The TiFeSi-type structure is a superstructure of the hexagonal phase with very nearly the same arrangement of atoms (Jeitschko, Acta Crystallogr. (1970) B26, 613), but results in the appearance of superconductivity in HfRuAs (Weimer, Phys. Lett. (1983) 95A, 163). The occurrence of the TiFeSi-type superstructure among the MX$_3$ ternary compounds with X = P, As, Si, or Ge correlates with Fe or Ru occupying the hexagonal $\text{M}$ site and consequently the underlying distortion can be rationalized as a sharing of unpaired electrons between pairs of Fe or Ru atoms. The nature of the distortion suggests superconductivity originates with the $\text{N}$-$\text{M}$-$\text{Si}$-$\text{M}$ chains which are present and undisorted in both superconducting modifications of ZrRu but are distorted in the non-superconducting modification of HfRuAs.

This work supported by US DOE.


The room temperature structures (22°C) of three crystal polymorphs of the compound 4,4'-bis(ethoxy)dioxyphehnetole (also called p,p'-azoxydiphenetole), a compound exhibiting a metastatic liquid crystalline phase from 137 to 168°C, as well as a low-temperature structure of the triclinic polymorph, have been determined. These structures represent the initial phase of a systematic variable temperature X-ray crystallographic study of several members of a homologous series (4,4'-bis(ethoxy)-, 4,4'-bis(eth­­oxy)-, and 4,4'-bis(propoxy)-azoxybenzene) in an attempt to obtain information regarding the intra- and inter-molecular interactions which must account for the liquid crystalline behavior of this series of compounds. The isolation of three crystal polymorphs at room temperature presents an opportunity to compare the intra- and inter-molecular interactions for this nonmetamagric molecule in these different packing arrangements. A comparison of the low- and room-temperature structures has been useful in extracting atomic thermal motion information from the somewhat disordered crystal structure of the triclinic polymorph.

05.227 The study by electron microscopy of virgin crystals (France and Fernández-Ferrer, 1984) obtained by evaporation from a water solution, shows two kind of crystals, which we have identified by X-ray powder analysis: 45 relevant peaks of diagrams are indexed according to the cell parameters of structure of ferroelectric phase of 105, and 41 with the cell parameters of switching fatigued structure.

The appearance of a ferroelectric phase at 105 in the virgin crystals suggest the possibility to remove a crystal and to freeze the previous crystal structure, because switching fatigued crystals show a lot of defects due to the aging process. The virgin ferroelectric phase has crystals with $\alpha_1=1.901(6), b=1.2, 682(6), c=5.751(7)$ and refined least to $R=0.026$ ($\text{R}=0.033$).

In order to determine the different morphology of crystals, a study by Hartmann-Peardock theory has been carried out. A first result has been that the crystallization ability of ferroelectric phase is less than ferroelectric one. This suggest to use a method of crystallization in which the ferroelectric phase would not be obtained. Experimental results show that ferroelectric phase does not growth in low supersaturation, while it is obtained to higher values of supersaturation.
05. PHYSICAL PROPERTIES AND STRUCTURE

05.2-29 GROWTH AND PROPERTIES OF PYROELECTRIC SINGLE CRYSTALS OF TETRAGONAL TUNGSTEN BRONZE STRUCTURE TYPE. By Ju. L.I. Leonyuk and N.I. Leonyuk, Department of Geology, Moscow State University, Moscow, USSR.

Crystal-chemical stability analysis is made for tetragonal tungsten-bronze structure type $A'$,$B_0^3B_0^3$,$A_0^2$ (where $A'$ and $A_0$ are large cations in five- and four-sided channels of the structure, $B_0$ are cations in three-sided channels, $B_0$ and $B_0'$ are multi-valent cations in two types of octahedra) in case when $A'$ are cations of alkaline and alkaline-earth metals.

Single crystals of some solid solutions of (Ba,Sr,Ca)Nb$_2$O$_6$ single crystals are studied. Curie temperatures and half-wave voltage values increase and dielectric constant at room temperature $\epsilon_{0}'$, widths of $\epsilon_{0}'$$(T)$ maxima and extent of broadening of ferroelectric phase transition decrease with increasing Ba contents in the crystals. Line widths of Gd$^{3+}$ ESR spectra in the crystals increase with increasing of phase transition broadening. Structural reasons of this are given.

05.2-30 RELATIONS BETWEEN THE STRUCTURE, MORPHOLOGY AND PHYSICAL PROPERTIES OF TRIGONAL AND MONOCLINIC TRA$_3$[BO$_3$]$_4$ CRYSTALS. I. I. Leonyuk and M. I. Leonyuk, Department of Geology, Moscow State University, Moscow, USSR.

Two structural types of TRA$_3$[BO$_3$]$_4$ crystals are known. The one, possessing a R32 space group (structural type of huitite) is more stable. It exists in the entire series of rare-earth-aluminium orthoborates. At temperatures exceeding 1270 K, TR-Al-Re compounds are crystallised according to the 0 2 0 space group as well.

There is a direct relationship between the development of hkl faces and the experimentally observed total intensity of X-rays reflected from the corresponding atomic lattices (e.g. 100$^\circ$+100$^\circ$+100$^\circ$+...+100$^\circ$). Faces (110), (110) and (010) of monoclinic crystals correspond to two trigonal primus(120) and (2110) in huitite-structured crystals. The base-pianocid (001) conforms to that having the same index in the trigonal crystal. The huitite rhombohedron (101) of the monoclinic crystal is represented by a rhombic prism (111) and pianocid (002). The relative significance of the faces in monoclinic crystals as compared with the trigonal ones is due to the peculiarities of their internal structure. TRA$_3$[BO$_3$]$_4$ crystals possess piezoelectric and nonlinear-optical properties. These properties vanish in the phase transition into the monoclinic modification.