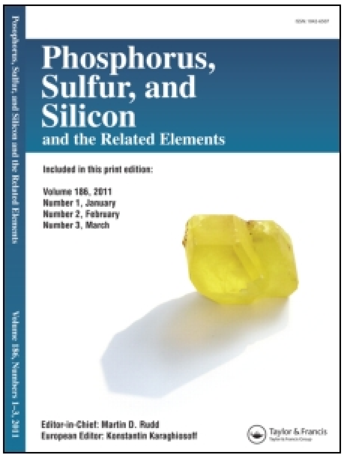

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Phosphides and Polyphosphides of the Transition Metals

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PHOSPHIDES AND POLYPHOSPHIDES OF THE TRANSITION METALS

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Abstract Many new phosphides and polyphosphides were obtained well crystallized by using a tin flux as reaction medium. Chemical bonding of the polyphosphides can be rationalized on the basis of classical two-electron bonds. This allows the prediction of the electrical conductivity behaviour and the magnetic properties. Atomic orbitals of the transition metal (T) atoms that are not required for bonding to the P atoms are either fully occupied by nonbonding electrons or form as many T-T bonds as possible. This is especially impressive for the compounds with composition TP_4, which crystallize in ten different structure types. In phosphides with a high metal content the P atom coordination is a tricapped trigonal prism. A large number of such compounds was prepared recently including ScCoP, $HoCo_3P_2$, $Sc_5Co_{19}P_{12}$, YCo_5P_3, $LaNi_5P_3$, $Ce_2Fe_{12}P_7$, and $LaCo_8P_5$. The compounds $Cu_2P_3I_2$ and $Ag_2P_3I_2$ are solid electrolytes with high mobility of the Cu^+ and Ag^+ ions.

INTRODUCTION

Although most binary systems of the transition elements with phosphorus have been investigated repeatedly in the past,[1,2] the use of previously rarely employed synthesis techniques has allowed the preparation of many new phosphides and polyphosphides. Besides high pressure techniques and the use of halogens for chemical transport, the employment of a tin flux is especially well suited for the synthesis of transition metal phosphides and polyphosphides in well crystallized form, thus making feasible their structural and physical characterization. Several recently characterized phosphides will be reviewed here.

POLYPHOSPHIDES WITH COMPOSITION TP_4 AND TT'_2P_{12}

Of the transition metal polyphosphides prepared in recent years the composition TP_4 occurs most frequently. A total of 15 polyphosphides TP_4 are known, which crystallize in 10 different structure types.[3-5] In these compounds the T atoms are always octahedrally surrounded by P atoms and attain oxidation number +2. All P atoms are tetrahedrally coordinated: one half of them to two T and two P atoms, the other half to one T and three P atoms. In stressing ionicity the P atoms may be considered as forming polyanions, which consist of two-dimensionally infinite networks of differently condensed 10-membered rings.

The TP_6 octahedra are linked by common corners and edges. T-T bonds occur via common edges in those compounds, where the T atoms have (low spin) d^3, d^4 and d^5 systems. In this way optimal use is made of all low energy valence orbitals: Two d orbitals ($\sim e_g$) participate in the formation of the six bonds to the P atoms ("d^2sp^3 hybrid"), and the other three ($\sim t_{2g}$) are either completely filled with nonbonding electrons (various modifications of the compounds FeP_4, RuP_4, OsP_4 with d^6 system) or they are partially filled with nonbonding electrons, while the remaining d orbitals overlap with the corresponding ones of neighbouring T atoms. In this way the T atoms with d^5 systems (three modifications of MnP_4; TcP_4, ReP_4) form T-T bonded pairs and the T atoms with d^4 systems (CrP_4, MoP_4) form infinite chains.

In agreement with these bonding characteristics most TP_4 compounds are diamagnetic semiconductors with band gaps between 0.2 and 0.6 eV. VP_4 with a d^3 system is electrondeficient. Consequently it is paramagnetic and its temperature dependence of the electrical conductivity is that of a metal.[5]

In order to extend the variations of the common building principles of the TP_4 compounds, we have investigated the pseudobinary sections TP_4-$T'P_4$. We have found several new compounds, however, in these the early transition metals T have always coordination number 8 (a square antiprism), while the other atoms have the expected environments. Like in the binary TP_4 compounds, however, the structural chemistry of the ternary TT'_2P_{12} ($TP_4 \cdot 2T'P_4$) compounds can completely be rationalized by classical two-electron bonds. Thus $MoFe_2P_{12}$ and isotypic WFe_2P_{12} are diamagnetic semimetals.[6] The MoP_8 (WP_8) and FeP_6 coordination polyhedra are linked only by common corners. The Mo(W) atoms obtain oxidation number +4 (d^2 system, "d^4sp^3 hybrid"), while Fe has again oxidation number +2.

In $TiMn_2P_{12}$, $NbMn_2P_{12}$, $MoMn_2P_{12}$ and WMn_2P_{12} the early transition metals have again oxidation number +4 and obtain d^0 (Ti), d^1 (Nb) or d^2 (Mo, W) systems.[7,8] The Mn atoms with oxidation number +2 ("low spin" d^5) saturate their spins by Mn-Mn bonds via common edges of the paired MnP_6 octahedra. Thus $TiMn_2P_{12}$, $MoMn_2P_{12}$ and WMn_2P_{12} are diamagnetic, while $NbMn_2P_{12}$ with one uncompensated spin on each Nb atom is paramagnetic.

$NbFe_2P_{12}$ crystallizes with a superstructure of $TiMn_2P_{12}$ caused by two different Fe-Fe distance, one bonding and one antibonding.[8] The compound can be rationalized as $(Nb^{+3})_2(Fe^{+3})_2(Fe^{+2})_2(P_{24})^{-16}$. It is diamagnetic, because the only d orbital of the Nb atoms, which is not participating in the Nb-P bonding, is doubly occupied by the two remaining valence electrons of the Nb atoms; the Fe^{+3} atoms with a d^5 system form Fe-Fe bonds like the Mn^{+2} atoms in $TiMn_2P_{12}$, and the Fe^{+2} atoms with a low-spin d^6 system do not carry a magnetic moment.

TERNARY RARE EARTH TRANSITION METAL PHOSPHIDES

A large number of ternary rare earth transition metal phosphides were prepared recently. Most of them have a metal/phosphorus ratio of 2:1 e.g. $ScCoP$,[9] $HoCo_3P_2$,[10] $Sc_5Co_{19}P_{12}$,[9] YCo_5P_3,[11] $LaNi_5P_3$[12] and $Ce_2Fe_{12}P_7$.[13] In these compounds the P atoms have a trigonal prismatic environment of metal atoms, which is augmented by three additional metal atoms outside the rectangular faces of the prism. The trigonal prisms are linked only via common edges. In $LaCo_8P_5$

with a slightly lower metal/phosphorus ratio,[14] some prisms share faces. The environments of the metal atoms show a great variety, reflecting their differing space requirements.

THE SOLID ELECTROLYTES $Cu_2P_3I_2$ AND $Ag_2P_3I_2$

The new compound $Cu_2P_3I_2$ is a diamagnetic semiconductor, where the P atoms form tubes similar to those of the Hittorf modification of phosphorus. They are surrounded by Cu atoms on 15 equipoint positions with occupancies varying between 15 and 97%. These in turn are surrounded by iodine atoms, which are well localized and form one-dimensional channels. The structural characteristics suggest high mobility of the Cu^+ ions. This was proven by an ion exchange reaction of the $Cu_2P_3I_2$ crystals in aqueous $AgNO_3$ solution, which forms the new isotypic compound $Ag_2P_3I_2$. Transference measurements in a cell $Ag/Ag_2P_3I_2/Ag$ show that the electrical conductivity is essentially due to the transport of Ag^+ ions.

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