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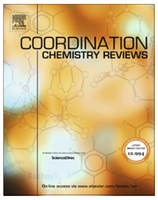

Review

A structural survey of the binary transition metal phosphides and arsenides of the *d*-block elements

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This article is dedicated to Pierre Braunstein on the occasion of his 70th birthday.

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ABSTRACT

This article presents a comprehensive review of the structures of the known structurally characterized transition metal (M) pnictide ($E = P$, As) compounds. These compounds are being widely studied for a range of important applications including magnetic materials, magnetocaloric effects, electric conductivity, and superconductivity in addition to high catalytic activities for reactions such as hydrodesulfurization, hydrodenitrogenation, and water splitting. A number of the M_xE_y combinations are found in mineral form, including meteorites. There is tremendous diversity in this class of compounds, with examples from early to late transition metals being observed having metal to main group element ratios (M:E) ranging from 7.5:1 to 1:10. The review covers 231 M:E stoichiometries crystallizing in 289 different crystal lattices. Compounds with high phosphorus or arsenic content show interesting catenated structures ranging from simple E_n units ($E = 2$–4), pyramidal —P(P)$_3$— groups, and P_6 rings to more complex branched chains, ribbons and 2-dimensional networks.

Contents

Abbreviations: M, transition metal; *E*, main group elements (in this review, phosphorus or arsenic); O_h, octahedron; TP, trigonal prism; mTP, monocapped trigonal prism; bTP, bicapped trigonal prism; tTP, tricapped trigonal prism; T_d, tetrahedron; bT_d, bicapped tetrahedron; SqPl, square planar; SqPy, square pyramid.

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1. Introduction

Transition-metal pnictides have attracted considerable attention because of their structural and compositional diversity that results in a range of desirable electronic, magnetic and catalytic properties [1–11]. Electronic and magnetic properties have not been fully explored for all of the compounds of this class of materials, and often pure samples of sufficient size have not been obtained to provide conclusive characterization. Consequently, there are often inconsistencies in the literature reports of these properties. Iron and nickel phosphides are known in meteorites but only rare examples have been found in the Earth's crust [12], and as much as 90% of the Earth's phosphorus may be tied up in the core, probably as metal phosphides [13]. There is a strong consistency in elemental compositions and structural trends of this class of materials. In spite of the changes in electron counts for the transition metals, for example, almost all of the first-row transition metals form 1:1 complexes with both phosphorus and arsenic. There are both similarities and variations in the crystal structures of these compounds, and the covalent character of the E—M bonding increases across the periodic table [3]. Phase diagrams for several transition metal phosphorus or arsenic systems have been reported [14–30]. A review of metal borides, silicides and phosphides appeared in 1965 and many of those bimetallic compounds (as well as other main group elements) have structures related to those of the metal pnictides [31].

The first structures of binary transition metal pnictides were reported in 1928 [32–34], followed by a slow but steady increase over the next few decades. Some of the early interest in the metal pnictides began in mineralogy with the study of naturally occurring pnictides such as the skutterudite ($CoAs_3$) phases and meteorites, where iron and nickel phosphides are common. These include melliniite: $(Ni,Fe)_4P$; schreibersite: $(Fe,Ni)_3P$; allabogdanite: orthorhombic $(Fe,Ni)_2P$; barringerite: hexagonal $(Fe,Ni)_2P$; monipite: MoNiP; florenskyite: FeTiP; and andreyivanonite: FeCrP. It is not possible to review synthetic methods extensively in this article due to space limitations, but a few comments are worthy of mention. Much of the early work on synthesizing metal pnictide materials was done through traditional solid-state methods, typically requiring heating the elements at temperatures in excess of 800 °C in glass or quartz tubes. In a number of cases, the reaction products were further subjected to arc melting in order to produce the final crystalline phases. Crystalline materials could be grown by vapor transport in some cases using iodine as a carrier. At elevated temperatures, volatilization of the main group elements could be limiting. The traditional solid-state methods, however, very strongly limit their utility in a wide variety of modern applications, especially those requiring formation of the compounds on substrates that would not survive harsh synthetic conditions. Considerable effort has been placed on the formation of metal pnictide nanoparticles using softer methods where much lower temperatures are needed [4,5,8,11,35–69]. In these cases, metal carbonyl or metal phosphine compounds as well as others have been decomposed to produce nanoparticles and thin films. Additionally, pre-formed metal nanoparticles can also be phosphidized upon suitable treatment with a phosphorus source such as phosphine or organophosphines.

In pursuing our goals of synthesizing phase pure materials for advanced applications, we were struck by the lack of a suitable reference work where these compounds are summarized and introduced to those entering the field. This article presents a comprehensive review (or as comprehensive as is feasible in a limited space) of the structural features of these compounds will be presented in the order of transition metal to pnictide ratio. Other organizational approaches could have been employed, such as coordination environments of the transition metals and/or pnictide elements, but these are far less regular and it is difficult to note trends from that organization. In order to increase the usefulness of the reference, we have included tables at the end that summarize the compounds not only by M:E ratio but grouped by transition metal so that the complete diversity of the metal pnictide

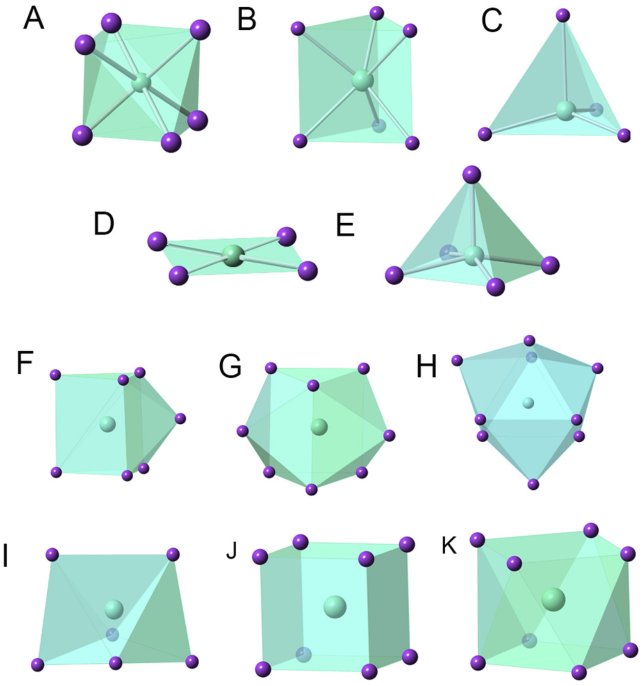

Fig. 1. Commonly observed metal coordination environments for M_xE_y compounds: (A) octahedron (triangular antiprism), (B) triangular prism, (C) tetrahedron, (D) square planar, and (E) square pyramid, (F) monocapped trigonal prism, (G) bicapped trigonal prism, (H) tricapped trigonal prism, (I) bicapped tetrahedron, (J) cube (square prism), and (K) square antiprism.

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