LiPN₂ AND NaPN₂ CRYSTALS:
STRUCTURAL FEATURES AND CHEMICAL BONDING

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The band structure spectra, densities of states, and valence and difference densities of LiPN₂ and NaPN₂ crystals were obtained by DFT self-consistent calculations using the nonlocal pseudopotentials and the localized pseudoorbital basis. Crystal-chemical analysis of these compounds shows that they occupy an intermediate position between the ideal structures of β-cristobalite and chalcopyrite, which manifests itself in the peculiarities of the electronic structure and chemical bonding. The valence band consists of three allowed subbands and differs radically from the typical valence band of chalcopyrite crystals in both subband structure and contributions of the s, p, and d atomic orbitals to the crystal orbitals.

Keywords: chalcopyrite, local density functional, sublattice, density of states, electron density, difference density, chemical bonding.

INTRODUCTION

According to the standard classification of substances, the ternary diamond-like compounds with a chalcopyrite structure are generally divided into chalcogenides 2ABC (anion atoms Æ = Ê, S, Se, Ɍɟ; cations A = Ag, Cu; and B = Al, Ga, In, Fe) and pnictides 2ABC (anion atoms Æ = N, Ɋ, As, and Sb; cations A = Mg, Zn, Cd; and B = Si, Ge, Sn).

The 2ABN class of pnictides differs substantially from 2ABC in composition, degree of tetragonal compression, and anion displacements from the fcc lattice sites. For this reason, they are called “highly compressed chalcopyrite-like compounds.”

In the 2ABN class of ternary compounds, only two compounds with an alkali metal atom, LiPN₂ [1-3] and NaPN₂ [4], were synthesized. They are interesting for both experimental and theoretical studies because of several peculiar features of their crystal structure.

The aim of the present work is a first principle calculation of the fundamental characteristics of the electronic structure of LiPN₂ and NaPN₂, analysis of chemical bonding in these compounds, and comparison of these characteristics with those of the known and well-studied crystals from the chalcopyrite family.

CRYSTAL CHEMISTRY OF LiPN₂ AND NaPN₂

The diamond-like compounds are distinguished by a tetragonal structure and four valence electrons per atom in the cation and anion sublattices. The conditions of the formation of A–B–C ternary systems are generally reduced to two inequalities [5],
where \( x \) is the probability of formation of a two-cation compound, and \( y \) is the same for a two-anion full valence ternary compound of \( A_{0.5-x}B_xC_{0.5} \) or \( A_{0.5}B_{0.5-x}C_x \) type.

For LiPN\(_2\) and NaPN\(_2\), the condition of the mean number of valence electrons per atom and the first inequality in (1) are valid. The latter indicates that a two-cation structure is possible for LiPN\(_2\) and NaPN\(_2\).

These compounds contain “tetrahedral cations” (P), i.e., the atoms that prefer the coordination number 4, and “nontetrahedral cations” (Li and Na). The possibility for the Li and Na cations to adopt a tetrahedral structure is realized via increased compression of the tetragonal \( c \) axis, which reaches \( 2 - (c/a) \), or 0.44 and 0.60 for LiPN\(_2\) and NaPN\(_2\), respectively. The latter may be called “chemical compression” in these systems because a compression as strong as this is due to the tendency for atoms to provide firm chemical bonding.

The topology of LiPN\(_2\) and NaPN\(_2\) is determined by the mutual arrangement of the PN\(_4\) tetrahedra and by the spatial net of the bonds of these tetrahedra [4]. These compounds are solid crystals consisting of a single three-dimensional net of P and N atoms formed by PN\(_4\) tetrahedra linked by angles. The alkali metal atoms lie between the tetrahedra. The change in the position of the tetrahedra is characterized by a rotation angle \( \varphi \), due to which one type of crystal changes into the other. The transition from the \( \beta \)-cristobalite (SiO\(_2\)) to ideal chalcopyrite structure is accompanied by rotation of the tetrahedron through an angle \( \varphi \) from 0° to 45° around the fourfold axis (\( \beta \)-cristobalite: \( \varphi = 0 \); NaPN\(_2\): \( \varphi = 26.4^\circ \); LiPN\(_2\): \( \varphi = 34.2^\circ \); ideal chalcopyrite: \( \varphi = 45^\circ \)). The distortion of the PN\(_4\) tetrahedron is determined by the P–N–P angle (NaPN\(_2\): 134°; LiPN\(_2\): 124°) [4]. Thus, the two compounds occupy an intermediate position between the \( \beta \)-cristobalite and chalcopyrite structures.

The structural parameters of LiPN\(_2\) and NaPN\(_2\) were obtained by X-ray diffraction [3, 4]. The compounds were found to be the isostructural analogs of chalcopyrite (space group \( D_{2d}^{12} \)). The lattice parameters and the atomic coordinates of nitrogen are \( a = 4.575(2) \) Å, \( c = 7.118(3) \) Å and \( (0.1699(31), 0.25, 0.125) \) for LiPN\(_2\); and \( a = 4.9721(2) \) Å, \( c = 6.9760(3) \) Å and \( (0.1293(1), 0.25, 0.125) \) for NaPN\(_2\). The chemical bonding was investigated by the sublattice method.

**CALCULATION PROCEDURE**

The first principle self-consistent calculations of the electronic structure of LiPN\(_2\) and NaPN\(_2\) were carried out using the local electron density formalism, the BHS pseudopotentials, and a basis of pseudoatomic \( sp^3d^2 \) orbitals expanded in series of plane waves. The total energy calculation converged to 0.01 au. The method and procedures for calculating the band structure, the density of states, and electron density distribution are described in detail in [6]. The chemical bonding was investigated by the sublattice method.

**ENERGY STRUCTURE AND NATURE OF ELECTRONIC STATES**

The energy spectrum of APN\(_2\) was calculated at the high symmetry points \( I(0, 0, 0), T(0, 0, 1), N(0.5, 0.5, 0), P(0.5, 0.5, 0.5) \) and along the lines connecting these points. The reference on the energy scale was chosen to be the position of the top of the valence band at the point \( T \) for LiPN\(_2\) and NaPN\(_2\). Near the top of the valence band there are secondary maxima within the limits of \(-1 \) eV at the points \( N \) and \( I \). The bottom of the conduction band lies at the point \( I \). Thus, both are indirect crystals. The presence of a valence band maximum at the point \( T \) confirms the hypothesis that the position of the energy level at the point \( T \) is determined by the tetragonal compression of the crystal and can be the fundamental maximum of the valence band at high compression [7]. The calculated densities of states \( N(E) \) for LiPN\(_2\) and NaPN\(_2\) crystals are presented in Fig. 1.