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PREDICTION OF COMPOUNDS RELATED TO $InFeZn_2O_5$

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The results of crystal-chemical analysis of layered hexagonal structures related to $InFeZn_2O_5$ and having space group $P6_3/mmc$ are reported. It was found that more than 250 new compounds could be synthesized. Multilayered compounds of other compositions are possible.

Keywords: crystal, hexagonal layered structures, prediction of compounds.

INTRODUCTION

Numerous oxide compounds of the general formula $(ABO_3)_n(MO)_m$, where A and B are trivalent metals; M is a divalent metal; and n and m are integers, have been synthesized [1]. The preparation and structural characterization of compounds with $n = 1$-4 and $m = 1$-19 were presented in a series of studies [2, 3]. A characteristic feature of these compounds is regular alternation of two space groups, $R\bar{3}m$ if both the n and m coefficients are odd and $P6_3/mmc$ if one of them is even. For compounds with paramagnetic iron ions, the characteristic magnetic properties related to the arrangement of the Fe^{2+} and Fe^{3+} ions in planar triangular nets and intense electron exchange between these two valence states were revealed. Some of these compounds, e.g., $ErFe_2O_4$ [4, 5], manifested structural transitions to low-symmetry phases depending on oxygen stoichiometry and were expected to be polar.

The $InFeZn_2O_5$ type of structure ($P6_3/mmc$, $Z = 2$) is common to these compounds. Other similar compounds are known with different compositions, for example, compounds with indium substituted by Lu, Yb, Tm, Ho, Er, and Y, with iron substituted by Mn, Ga, and Al, and with zinc replaced by Co, Fe, Mn, Cu, and Mg [2, 3, 6].

$InFeO_3(ZnO)_m$ were synthesized ($m = 1$-19) [2, 3, 6]; their formation can be described by the reaction $InFeO_3 + m{\cdot}ZnO = InFeO_3(ZnO)_m$. The layered nature of the compounds is not well expressed in the structures. Sometimes, close overlapping of layers is possible in several ways, only slightly differing in energy, and diverse modifications of such structures are frequent. This example is not unique.

The formation of compounds containing few layers of divalent metals can be represented by the reaction $ABX_3 + m{\cdot}MX = ABM_mX_{m+3}$. In our case, this is $InFeO_3 + 2ZnO = InFeZn_2O_5$. This example reveals some regularities better. The starting components have the following structures,

Compound	Space group	Z	a, Å	c, Å	Reference
$InFeO_3$	$P6_3/mmc$	2	3.334	12.202	[7]
ZnO	$P6_3mc$	2	3.25	5.206	[6, 8]

(Z is the number of formula units in the unit cell of the structure).

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ZnO has a structure of ZnS (wurtzite), where all positions occupied by the atoms of each of the elements constitute a regular system of points. Both systems occupied by the sulfur and zinc atoms are equivalent, as in the case of the NaCl, CsCl, and other types of structure. This structural type is often referred to as ZnO [8]. Wurtzite is characterized by piezoelectric properties. There are several modifications of wurtzite, which differ in the order of alternation of layers in the direction perpendicular to the principal crystallographic axis *c*. The simplest variant, wurtzite itself, is hexagonal double-layered; besides, there are four- and six-layered hexagonal modifications, as well as three- and fifteen-layered rhombohedral ones [9].

PREDICTION OF NEW COMPOUNDS

The structures of $InFeO_3(ZnO)_m$ can be considered as systems originating from the intergrowth of two structural types, $InFeO_3$ and ZnO (wurtzite).

Some regularities in the development of the structures can be illustrated by the structures of the starting components. All compounds involving indium have the *a* unit cell parameter varying from 3.321 Å ($InFeZnO_4$) to 3.263 Å ($InFeZn_{19}O_{22}$); i.e., they fall within the range of the related parameters of the starting structures. This means that the intergrowth of the original cells occurs in the *a*-*b* basal planes. Additionally, for $InFeO_3(ZnO)_m$ the unit cell parameter along the principal axis equals the sum of the *c* parameters of the starting components taken in proportion to their molar fractions in the unit cell.

Thus, for $InFeOZn_{19}O_{22}$ containing 19 layers of ZnO, the calculated parameter is $c = (c_{InFeO_3} + mc_{ZnO})\times(z/2) = (12.202 + 5.206\times19)\times1.5 = 166.67$ Å, the experimental value being 166.5 Å. The difference is +0.1%. The intergrowth of the starting components of the $InFeO_3$ and ZnO types involves entire unit cells. Indeed, this can explain the formation of layered hexagonal structures including several layers of $InFeO_3$ and one layer of ZnO, as well as several layers of ZnO and one layer of $InFeO_3$.

From the viewpoint of packing, layered structures with an arbitrary number of layers in the unit cell can be synthesized in this system. As there are no restrictions on the number of layers, multilayered structures can be anticipated where single-layered ones are known.

Earlier, compounds of $YbFe_2O_4$ and $Yb_2Fe_3O_7$ types were analyzed and predicted [10, 11], and it was revealed that more than 220 new crystals could be synthesized.

The above compositions include ABX_3 compounds as the starting components, which are structurally similar to perovskite but have hexagonal or distorted perovskite type structures. The structures with large *m* contain a lot of ZnO, which is not surprising because the wurtzite type structure is known to give polytypes [9]. In other (zinc-free) compositions, the (MO) component has a NaCl type structure. The ability of this structural type to form intermediate blocks was proved by results of the synthesis of numerous perovskite-like compounds [12, 13].

Stacks and blocks are easily discernible on the structure drawings for perovskite-like layered structures, but not for the hexagonal and rhombohedral structures. The elements of the starting phases can be revealed in the structures, but the boundaries of intergrowth of the original cells are still to be elucidated.

The structures exhibit specific and general features. The A cation has an octahedral anionic environment ($cn_A = 6$). The other cations have a fivefold environment, namely, a trigonal bipyramid (it can be considered as inherited from the $InFeO_3$ prototype).

All the structures are formed from AX_6 and BX_5 polyhedra combined in different ways. Based on the Shannon ionic radii [14], fivefold coordination should mostly be expected for B^{3+} = Fe, Mn, Ga, and Al, which are just the atoms that are involved in the synthesized compounds. Among B^{2+}, Ni, Co, Fe, Mn, Cu, and Mg are possible; cn 6 is possible for Y, Sc, Ta, and many rare-earth elements.

The anticipated areas of formation of $InFeZn_2O_5$ type structures are presented in Tables 1 and 2. The rows include the cations that form octahedra, and the columns are the cations that make trigonal bipyramids. The crossing of a row and a column yields the composition of a known or predicted compound. The borders of the areas were primarily determined from the compositions of known compounds.

TABLE 1. Prediction of $InFeZn_2O_5$ Type Compounds with ABC_2O_5 ($A^{3+}B^{3+}C_2^{2+}O_5^{2-}$) Compositions

$B^{3+}\rightarrow$	Ga						Fe						Al					
$C^{2+}\rightarrow$	Co	Fe	Mn	Cu	Zn	Mg	Co	Fe	Mn	Cu	Zn	Mg	Co	Fe	Mn	Cu	Zn	Mg
$A^{3+}\downarrow$																		
La																		
Y			▲															
Sc					▲						▲						▲	
Tl																		
In			▲		▲	▲					▲			▲			▲	▲
Ce																		
Pr																		
Nd																		
Pm																		
Sm																		
Eu																		
Gd																		
Tb																		
Dy																		
Ho			▲															
Er			▲															
Tm			▲		▲	▲					▲						▲	
Yb			▲		▲	▲					▲						▲	
Lu			▲		▲						▲							

▲ — known compounds, ▭ — area of possible new compounds.

CONCLUSIONS

This contribution was stimulated by the request for prediction of novel compounds related to the structure of $InFeZn_2O_5$. It is evident from Tables 1 and 2 that more than 250 new compounds can be synthesized. But the number of possible compounds is much larger. The middle part of Tables 1 and 2 includes the elements Ce-Dy. Their radii exceed the radius of the Ho^{3+} holmium cation, for which the structure $HoGaMn_2O_5$ is known, by only 0.1 Å. New multilayered compounds can be synthesized. As ZnO is prone to formation of polytypes, novel layered structures can develop for the $ABO_3(ZnO)_m$ compositions.

The physical properties of these crystals were examined only scarcely yet. We are aware of only few studies [4, 5, 15-17]. A combination of the B^{3+} and B^{2+} cations in the anionic polyhedra is realized in these structures. This structural peculiarity can give rise to specific physical properties. New laser crystals can be synthesized among the predicted compositions. These crystal structures have large distances between the A–A positions, large unit cell volumes, and can include rare-earth active dopants.

TABLE 2. Prediction of $InFeZn_2O_5$ Type Compounds with $ABCZnO_5$ Compositions

$B^{3+}\rightarrow$	Ga					Fe					Al				
$C^{2+}\rightarrow$	Co	Fe	Mn	Cu	Mg	Co	Fe	Mn	Cu	Mg	Co	Fe	Mn	Cu	Mg
$A^{3+}\downarrow$															
La															
Y															
Sc	▲				▲						▲				▲
Tl															
In	▲				▲	▲	▲			▲	▲				▲
Ce															
Pr															
Nd															
Pm															
Sm															
Eu															
Gd															
Tb															
Dy															
Ho															
Er															
Tm					▲					▲					
Yb					▲					▲					▲
Lu					▲					▲					▲

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