

## PREDICTIONS OF COMPOUNDS IN THE FAMILY OF DELAFOSSITES

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UDC 548.3

This paper reports the results of our crystal-chemical analysis of structures from the delafossite family  $A^+B^{3+}X_2$ , where A and B are cations, and X is oxygen. The family is represented by structures of two types,  $CuFeO_2$  and  $\alpha\text{-NaFeO}_2$  ( $R\bar{3}m$ ,  $Z = 1$ ). Predictions of new compounds are presented. About a hundred new crystals can be synthesized.

**Keywords:** crystal, structural family of delafossite, predictions of new compounds.

### INTRODUCTION

The  $ABX_2$  oxides have a number of useful physical properties. In  $PdCoO_2$  ( $Pd^{1+}$ ,  $Co^{3+}$ ), the Pd–Pd interatomic interactions are responsible for very high electric conductivity, which is comparable to that of copper [1].  $PtCoO_2$  also has high electric conductivity.  $ABX_2$  crystals with a  $\alpha\text{-NaFeO}_2$  type structure are promising semiconductors [2]. Lithium cobaltite ( $Li_xCoO_2$ ) can serve as an effective cathode material for chemical sources of current [3]. Geisler alloys are known for  $ABX_2$  [2, 4] and are of interest for studying the nature of the ferromagnetic state.  $M LnO_2$  crystals ( $M = Li, Na, K$ ;  $Ln = Y, Gd$ ) activated by  $Eu^{3+}$  ions luminesce at 500–400 nm [5].

The aim of this work is to perform crystal-chemical analysis of the structures of  $A^+B^{3+}X_2$  and evaluate the possibilities for the synthesis of new compounds.

### STRUCTURES IN THE DELAFOSSITE FAMILY

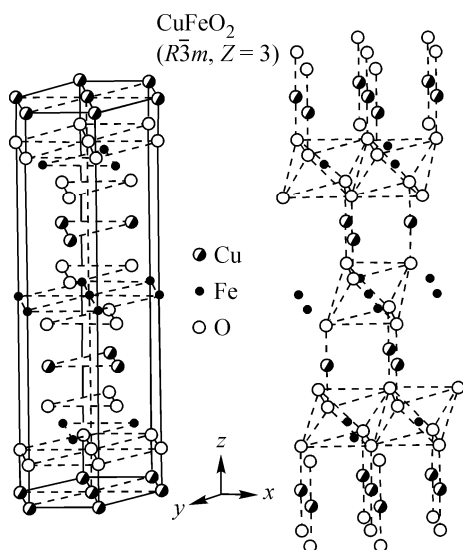
Delafossite is a mineral of the general formula  $CuFeO_2$ , which received the name of the French crystallographer of the 19th century G. Delafosse [6]. It has a rhombohedral structure with a space group  $R\bar{3}m$ . The primitive rhombohedral cell has one  $ABX_2$  formula unit,  $Z = 1$ ; in the hexagonal setting,  $Z = 3$ . These structures are generally denoted by  $F5_1$ . In the literature, they are denoted by the formulas of different prototypes, namely,  $CuFeO_2$ ,  $\alpha\text{-NaFeO}_2$ ,  $NaHF_2$ ,  $NaCrS_2$ ,  $CuCrO_2$ , and  $CuLaO_2$  [7–9]. Visualization of the rhombohedral phases of these compounds revealed differences in their structures [10]. The six structures above can be grouped in the following way:

- 1)  $CuFeO_2$ ,  $CuCrO_2$ ,  $CuLaO_2$ , and  $HNaF_2$  structures; and
- 2)  $\alpha\text{-NaFeO}_2$  and  $NaCrS_2$  structures.

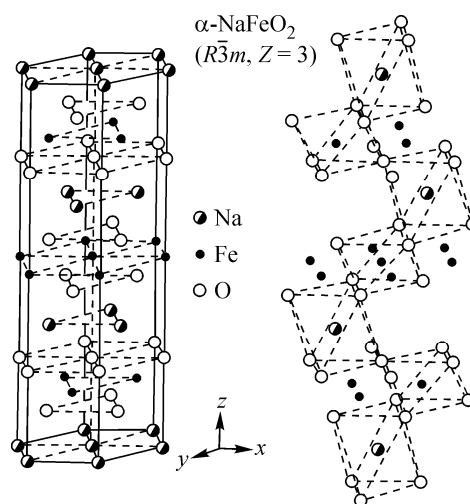
The structures presented in Table 1 have a rhombohedral space group  $R\bar{3}m$ , the corresponding cations occupying the equivalent points of this space group. The only difference is observed in the starting relative coordinates of oxygen atoms.

**TABLE 1.** Structural Parameters of Prototypes in the Family of Delafossites

CuFeO <sub>2</sub>			$(R\bar{3}m, Z = 3)$			$a = 3.0651 \text{ \AA}$			$c = 17.166 \text{ \AA}$			[9, 11]					
$\alpha$ -NaFeO <sub>2</sub>			$(R\bar{3}m, Z = 3)$			$a = 3.022 \text{ \AA}$			$c = 16.082 \text{ \AA}$			[9]					
Atomic positions			CuFeO <sub>2</sub>			$\alpha$ -NaFeO <sub>2</sub>			Atomic positions			CuFeO <sub>2</sub>			$\alpha$ -NaFeO <sub>2</sub>		
Atom	Position	No.	$x/a$	$y/b$	$z/c$	$x/a$	$y/b$	$z/c$	Atom	Position	No.	$x/a$	$y/b$	$z/c$	$x/a$	$y/b$	$z/c$
A	3a	1	0	0	0	0	0	0	X	6c	7	0	0	0.107	0	0	0.237
		2	1/3	1/3	2/3	1/3	1/3	2/3			8	0	0	0.893	0	0	0.769
		3	2/3	1/3	1/3	2/3	1/3	1/3			9	1/3	2/3	0.774	1/3	2/3	0.898
B	3b	4	0	0	1/2	0	0	1/2			10	1/3	2/3	0.560	1/3	2/3	0.436
		5	1/3	2/3	0.167	1/3	2/3	0.167			11	2/3	1/3	0.440	2/3	1/3	0.564
		6	2/3	1/3	0.833	2/3	1/3	0.833			12	2/3	1/3	0.226	2/3	1/3	0.102



**Fig. 1.** Structure of CuFeO<sub>2</sub>.



**Fig. 2.** Structure of  $\alpha$ -NaFeO<sub>2</sub>.

At first sight, it seems these are identical structures that should be formed for the coordinates of oxygen atoms  $z/c$  from 0.1 to 0.3. However, the structures differ in the coordination of cations and have the coordination formulas Cu<sup>II</sup>Fe<sup>VI</sup>O<sub>2</sub>, Na<sup>VI</sup>Fe<sup>VI</sup>O<sub>2</sub> (with coordination numbers as the upper indices). Figures 1 and 2 show the structures in the hexagonal setting. They should be regarded as prototypes in the  $F5_1$  family.

Thus, all structures in the  $F5_1$  family have identical cation sublattices. The cations occupy the special positions, and their relative coordinates are constant. The coordinates of the anions can change. The structures have no mixed cation–anion layers. The coordinates of anions, therefore, cannot coincide with those of cations. In the  $F5_1$  family, structures can only form with limited compositions. The initial coordinates of anions can be  $z/c = 0.10$ – $0.12$  for CuFeO<sub>2</sub> and  $z/c = 0.22$ – $0.29$  for  $\alpha$ -NaFeO<sub>2</sub>.

## PHASE TRANSITIONS

Structural phase transitions were reported for crystals from the given family. In NaFeO<sub>2</sub>, the  $\alpha$  modification is a low-temperature phase. In the high-temperature ( $\beta$ ) phase of NaFeO<sub>2</sub>, the cations have tetrahedral environments. The tetrahedra are linked by their vertices. These phases are known for LiGaO<sub>2</sub> [12] and AgAlO<sub>2</sub> [13]. Transitions of this kind are inherent in crystals in which trivalent cations are relatively small.

If the trivalent cation is large ( $(R_A/R_B) > 1.62$ ) (rare-earth cation), the high-temperature phase can be hexagonal, of  $\beta$ -RbScO<sub>2</sub> type ( $R_A$  and  $R_B$  are the ionic radii of the A and B atoms according to Shannon's system [14]). The low-temperature modification in RbScO<sub>2</sub> is rhombohedral, of  $\alpha$ -NaFeO<sub>2</sub> type. In  $\beta$ -RbScO<sub>2</sub>, the coordination number (c.n.) of rubidium is 6 (trigonal prism); c.n.<sub>Sc</sub> is 6 (octahedron). At  $(R_A/R_B) = 1.13$ -1.17,  $\alpha$ -NaFeO<sub>2</sub> is a high-temperature phase. In the low-temperature phases, NaCl type cubic structures with a statistical arrangement of cations are formed.

In LiTiO<sub>2</sub> ( $(R_A/R_B) = 0.86$ ), a cubic structure of NaCl type is a high-temperature phase above 640°C. The crystal lattice is tetragonal ( $I4_1/amd$ ) at 640-570°C and rhombohedral at 570-480°C [1].

The majority of structural transitions are intrinsic in prophanes of  $\alpha$ -NaFeO<sub>2</sub> type. We did not find any examples of low-temperature phases for delafossite (CuFeO<sub>2</sub>) type compounds; at elevated temperatures, they can become hexagonal phases of  $\delta$ -AgFeO<sub>2</sub> type.

In ABX<sub>2</sub> compositions with NaCl type structures and statistical distributions of large cations, phase transitions occur above 300-400°C and result in  $\alpha$ -NaFeO<sub>2</sub> type structures with lower symmetry and ordering of atoms [1].

### PREDICTION OF NEW A<sup>+</sup>B<sup>3+</sup>O<sub>2</sub> COMPOUNDS

Table 2 lists the predicted structures in the family of delafossite (bold type). The lines present the univalent cations, and the columns show the trivalent cations. The cells found at the intersections of lines and columns correspond to the chemical compositions of known or hypothetical compounds. All cations were divided into groups according to their chemical properties and the types of their electron shells. In groups, the cations are arranged according to their size. While making predictions, we took into account the ratio between the radii of cations ( $R_A/R_B$ ) and the presence of known "neighboring" structures.

TABLE 2. Structures and Predictions of A<sup>+</sup>B<sup>3+</sup>O<sub>2</sub>

A <sup>+</sup> ↓	B <sup>3+</sup> →	Ni	Co	Cr	V	Fe	Mn	Ti	Ga	In	Tl	←B <sup>3+</sup>
Cs	HTP											Cs
	LTP								<i>r</i>	<i>t</i>	<i>rh2, t</i>	
Rb	HTP											Rb
	LTP		<i>r</i>	<i>r</i>		<i>r</i>	<i>r</i>		<i>r</i>	<b>rh2</b>	<i>rh2</i>	
K	HTP							<b>h2</b>	<b>h2</b>	<b>h2</b>	<b>h2</b>	K
	LTP		<i>t</i>	<i>rh2</i>	?	<i>c, r</i>	<i>m</i>	<b>rh2</b>	<i>r</i>	<b>rh2</b>	<i>rh2</i>	
Na	HTP	<i>rh2</i>				<i>c2</i>	<i>r</i>				<i>rh2</i>	Na
	LTP	<i>m</i>	<i>rh2, h</i>	<i>rh2</i>	<i>rh2</i>	<i>rh2</i>	<i>rh2</i>	<i>rh2</i>	<b>rh2</b>	<i>rh2, c2</i>	<i>c2</i>	
Li	HTP					<i>c2</i>					<i>c2</i>	Li
	LTP	<i>rh2</i>	<i>rh2</i>	<i>rh2</i>	<i>rh2, r</i>	<i>t2, rh2</i>	<i>r, m</i>	<i>c2</i>	<i>rh2, r8</i>	<i>t2</i>	<i>t2, r</i>	
Tl	HTP											Tl
	LTP	<i>c2</i>						<b>rh2</b>	<b>rh2</b>	<b>rh2</b>	<b>rh2</b>	
In	HTP											In
	LTP							<b>rh2</b>	<b>rh2</b>	<b>rh2</b>	<b>rh2</b>	
Ag	HTP					<i>r8</i>					<i>h1</i>	Ag
	LTP	<i>rh1</i>	<i>rh1</i>	<i>rh1</i>	<b>rh1</b>	<i>rh1</i>	<b>rh1</b>	<b>rh1</b>	<i>r8</i>	<i>rh1</i>	<i>rh1</i>	
Cu	HTP	<b>h1</b>	<b>h1</b>	<b>h1</b>	<b>h1</b>	<b>h1</b>	<b>h1</b>	<b>h1</b>	<b>h1</b>	<b>h1</b>	<b>rh1</b>	Cu
	LTP	<b>rh1</b>	<i>rh1</i>	<i>rh1</i>	<b>rh1</b>	<i>rh1</i>	<b>rh1</b>	<b>rh1</b>	<i>rh1</i>	<i>rh1</i>	<i>rh1</i>	
Pd	LTP	<b>rh1</b>	<i>rh1</i>	<b>rh1</b>								Pd
Pt	LTP	<b>rh1</b>	<i>rh1</i>	<b>rh1</b>								Pt

TABLE 2. (Continued)

A <sup>↓</sup>	B <sup>3+</sup> →	Al	Sc	Y	La	Mo	Nb	Ta	Pd	Rh	Ru	←B <sup>3+</sup>
Cs	HTP			<i>h2</i>	<i>h2</i>							Cs
	LTP		<i>c*</i>	<i>rh2</i>	<i>rh2</i>							Rb
Rb	HTP		<i>h2</i>									Rb
	LTP		<i>rh2</i>	<i>rh2</i>	<i>rh2</i>							K
K	HTP	<b><i>h2</i></b>	<i>h2</i>	<b><i>h2</i></b>	<b><i>h2</i></b>							K
	LTP	<b><i>rh2</i></b>	<i>rh2</i>	<i>rh2</i>	<i>rh2</i>							Na
Na	HTP		<i>rh2</i>	<i>rh2</i>								Na
	LTP	<i>r8, rh</i>	<i>c2</i>	<i>c2, m</i>	<i>t2</i>	<i>h, rh</i>			<b><i>rh2</i></b>	<i>rh2</i>	<b><i>rh2</i></b>	Li
Li	HTP	<i>r8</i>								<i>c?</i>		Li
	LTP	<i>rh2</i>	<i>t2</i>	<i>t2, m</i>	<i>r, m</i>	<i>rh</i>	<i>r</i>			<i>rh2</i>	<i>r</i>	Tl
Tl	HTP											Tl
	LTP	<b><i>rh2</i></b>	<b><i>rh2</i></b>	<b><i>rh2</i></b>	<b><i>rh2</i></b>							In
In	HTP											In
	LTP	<b><i>rh2</i></b>	<b><i>rh2</i></b>	<b><i>rh2</i></b>	<b><i>rh2</i></b>							Ag
Ag	HTP											Ag
	LTP	<i>r8</i>								<i>rh1</i>		Cu
Cu	HTP			<i>h</i>	<b><i>h1</i></b>							Cu
	LTP	<i>rh1, h</i>	<i>h</i>	<i>rh1</i>	<i>rh1</i>				<i>t</i>	<b><i>rh1</i></b>		Pd
Pd	LTP											Pd
Pt	LTP											Pt

A <sup>↓</sup>	B <sup>3+</sup> →	Lu	Yb	Tm	Er	Ho	Dy	Tb	Gd	Eu	Sm	Pm	Nd	Pr	Ce
Cs	HTP	<i>h2</i>	<i>h2</i>	<i>h2</i>	<i>h2</i>	<i>h2</i>	<i>h2</i>	<i>h2</i>	<i>h2</i>	<i>h2</i>	<i>h2</i>	<b><i>h2</i></b>	<i>h2</i>	<i>h2</i>	<b><i>h2</i></b>
	LTP	<i>rh2, t4</i>	<i>rh2</i>	<i>rh2</i>	<i>rh2</i>	<i>rh2</i>	<i>rh2</i>	<i>rh2</i>	<i>rh2</i>	<i>rh2</i>	<i>rh2</i>	<b><i>rh2</i></b>	<i>rh2</i>	<i>rh2</i>	<b><i>rh2</i></b>
Rb	HTP														
	LTP	<b><i>rh2</i></b>	<b><i>rh2</i></b>	<b><i>rh2</i></b>	<b><i>rh2</i></b>	<b><i>rh2</i></b>	<b><i>rh2</i></b>	<b><i>rh2</i></b>	<b><i>rh2</i></b>	<b><i>rh2</i></b>	<b><i>rh2</i></b>	<b><i>rh2</i></b>	<b><i>rh2</i></b>	<b><i>rh2</i></b>	<b><i>rh2</i></b>
K	HTP														
	LTP	<b><i>rh2</i></b>	<i>rh2</i>	<b><i>rh2</i></b>	<i>rh2</i>	<i>rh2</i>	<i>rh2</i>	<i>rh2</i>	<i>rh2</i>	<i>rh2</i>	<i>rh2</i>	<b><i>rh2</i></b>	<i>rh2</i>	<i>rh2</i>	<i>rh2</i>
Na	HTP	<i>rh2</i>	<i>rh2</i>	<i>rh2</i>	<i>rh2</i>	<i>rh2</i>	<i>rh2</i>	<i>t2</i>	<i>t2</i>	<i>t2</i>	<i>t2</i>		<i>t2</i>		
	LTP	<i>c2</i>	<i>c2</i>	<i>c2</i>	<i>c2, m</i>	<i>c2, m</i>	<i>c2, m</i>	<i>c2</i>	<i>c2</i>	<i>c2</i>	<i>c2</i>	<b><i>c2</i></b>	<i>c2</i>	<i>t2</i>	<i>t2</i>
Li	HTP														
	LTP	<i>t2</i>	<i>t2</i>	<i>t2</i>	<i>t2</i>	<i>m, t</i>	<i>t, m</i>	<i>r, m5</i>	<i>r,</i>	<i>t, r, m</i>	<i>r, m5</i>		<i>m5</i>	<i>m5</i>	<i>m?</i>
Tl	LTP	<b><i>rh2</i></b>	<b><i>rh2</i></b>	<b><i>rh2</i></b>	<b><i>rh2</i></b>	<b><i>rh2</i></b>	<b><i>rh2</i></b>	<b><i>rh2</i></b>	<b><i>rh2</i></b>	<b><i>rh2</i></b>	<b><i>rh2</i></b>	<b><i>rh2</i></b>	<b><i>rh2</i></b>	<b><i>rh2</i></b>	<b><i>rh2</i></b>
In	LTP	<b><i>rh2</i></b>	<b><i>rh2</i></b>	<b><i>rh2</i></b>	<b><i>rh2</i></b>	<b><i>rh2</i></b>	<b><i>rh2</i></b>	<b><i>rh2</i></b>	<b><i>rh2</i></b>	<b><i>rh2</i></b>	<b><i>rh2</i></b>	<b><i>rh2</i></b>	<b><i>rh2</i></b>	<b><i>rh2</i></b>	<b><i>rh2</i></b>
Ag	LTP	<i>rh1</i>	<i>rh1</i>	<i>rh1</i>	<i>rh1</i>	<b><i>rh1</i></b>	<b><i>rh1</i></b>	<b><i>rh1</i></b>	<b><i>rh1</i></b>	<b><i>rh1</i></b>	<b><i>rh1</i></b>	<b><i>rh1</i></b>	<b><i>rh1</i></b>	<b><i>rh1</i></b>	<b><i>rh1</i></b>
Cu	LTP	<b><i>rh1</i></b>	<b><i>rh1</i></b>	<b><i>rh1</i></b>	<b><i>rh1</i></b>	<b><i>rh1</i></b>	<b><i>rh1</i></b>	<b><i>rh1</i></b>	<b><i>rh1</i></b>	<b><i>rh1</i></b>	<b><i>rh1</i></b>	<b><i>rh1</i></b>	<b><i>rh1</i></b>	<b><i>rh1</i></b>	<b><i>rh1</i></b>

Notes. HTP is the high-temperature phase; LTP is the low-temperature or room-temperature phase.

Type	Structure
<i>c2</i> — NaCl	<i>c</i> — cubic
<i>h1</i> — $\delta$ -AgFeO <sub>2</sub>	<i>h</i> — hexagonal
<i>h2</i> — $\beta$ -RbScO <sub>2</sub>	<i>rh</i> — rhombohedral
<i>rh1</i> — CuFeO <sub>2</sub> (delafossite)	<i>t</i> — tetragonal
<i>rh2</i> — $\alpha$ -NaFeO <sub>2</sub>	<i>r</i> — orthorhombic
<i>t2</i> — $\alpha$ -LiFeO <sub>2</sub>	<i>m</i> — monoclinic without refinement
<i>r8</i> — $\beta$ -NaFeO <sub>2</sub>	of the structural type
<i>m5</i> — $\delta$ -LiSmO <sub>2</sub>	? — synthesized compound with an unknown structure

The Hg<sup>+</sup>, Pb<sup>+</sup>, and Au<sup>+</sup> lines were excluded from the table because ABX<sub>2</sub> compounds with these elements are not known. The ABX<sub>2</sub> compounds with B<sup>3+</sup> = N, B, P, As, Bi, Cu, Br, Ag, Au were excluded for the same reason.

The prediction of  $\text{Tl}^+\text{BO}_2$  compounds can be substantiated as follows. These compounds are possible from the geometrical viewpoint because the radius of univalent thallium is comparable to the radius of rubidium. Among the known structures of rubidium are  $\alpha\text{-NaFeO}_2$  type structures. The compound  $\text{Tl}_3^+\text{Tl}^{3+}\text{O}_3$  was synthesized in an inert gas atmosphere at  $450^\circ\text{C}$ . The presence of this compound was confirmed by crystallization in the  $\text{Tl}_2\text{O-Tl}_2\text{O}_3\text{-H}_2\text{O}$  system at  $25^\circ\text{C}$  [1]. Therefore, compounds with univalent thallium in combination with other sesquioxides will hopefully be obtained in future.

## CONCLUSIONS

The results of our analysis show that about a hundred compounds with delafossite-like structures can be synthesized. The number of delafossite-like compounds, however, will be more than that, especially in compositions with univalent palladium and platinum. In Rb, K, and rare-earth compounds, high-temperature phases are possible. A number of crystal-chemical laws can be used in the selective search for and synthesis of new objects of studies.

$\text{CuFeO}_2$  type structures with  $\text{A}^+ = \text{Ag, Cu, Pd, Pt}$  are known and evidently possible for  $\text{A}^+ = \text{Au}$ . For known structures of this type,  $(R_A/R_B) = 0.45\text{-}1.10$ . The ratio  $z/c$  for the anion in  $\text{CuFeO}_2$  type structures is almost constant and determined by the sum of the radii  $(R_A + R_X)/c$  and cannot be smaller than 0.1 and larger than 0.12 for oxides. In  $\text{CuFeO}_2$  type compounds, increased electric conductivity and thermal conductivity are possible; at elevated temperatures, they can become  $\delta\text{-AgFeO}_2$  type hexagonal.

In  $\alpha\text{-NaFeO}_2$  type crystals, there may be phase transitions to NaCl type low-temperature phases at  $(R_A/R_B) = 1.13\text{-}1.37$  and  $\beta\text{-RbScO}_2$  type high-temperature hexagonal phases at  $(R_A/R_B) > 1.60$  [15].

Among  $\text{ABX}_2$  sulfides and selenides, there are few compounds with delafossite-like structures. New compounds of  $\alpha\text{-NaFeO}_2$  type for these systems were predicted by N. N. Kiseleva and E. M. Savitskii [16, 17].

This work was carried out at the Crystal Physics Laboratory, L. V. Kirenskii Institute of Physics, Siberian Division, Russian Academy of Sciences under program No. 2.5 OFN RAN "New Materials and Structures" and the President of RF Program of support for the leading scientific schools of the Russian Federation (grant No. NSH-4137.2006.2).

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