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Prediction of New $A^+B^{+3}X_2^{+5}O_7$ Compounds

N. N. Kiselyova[a], *, A. V. Stolyarenko[a], V. V. Ryazanov[b], O. V. Sen'ko[b], and A. A. Dokukin[b]

[a] *Baikov Institute of Metallurgy and Materials Science, Russian Academy of Sciences, Moscow, 119334 Russia*
[b] *Federal Research Center "Informatics and Management," Russian Academy of Sciences, Moscow, 119333 Russia*
**e-mail: kis@imet.ac.ru*

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Abstract—Hitherto unprepared compounds of composition ABX_2O_7 (where A^+ and B^{3+} are different cations; and X = P^{5+}, V^{5+}, As^{5+}, Nb^{5+}, Sb^{5+}, or Ta^{5+}) are predicted. Criteria are found to predict the possibility for these compounds to crystalize in one of the crystal structure types ($KAlP_2O_7$, weberite, $NaAlP_2O_7$, $LiFeP_2O_7$, or pyrochlore) at room temperature and atmospheric pressure. The prediction is based only on the properties of elements and simple oxides. The average prediction accuracy is at least 88%. The calculations use an information-analytical system (IAS) comprising precedent-based pattern recognition software.

Keywords: oxides with the $KAlP_2O_7$ crystal structure, weberite, $NaAlP_2O_7$, $LiFeP_2O_7$, pyrochlore, precedent-based pattern recognition

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Compounds ABX_2O_7 (where A^+ and B^{3+} are different cations; and X = P^{5+}, V^{5+}, As^{5+}, Nb^{5+}, Sb^{5+} or Ta^{5+}) are of interest for the search for new ferroelectric [1], magnetic [2], and luminescent [3, 4] materials, catalysts [5, 6], cathode materials for lithium batteries [7, 8], etc.

According to the data compiled in the PHASES database [9], the greatest number of compounds of this composition were synthesized in phosphate systems (Fig. 1). Most ABP_2O_7 compounds under ambient conditions (at room temperature and atmospheric pressure) crystallize in $KAlP_2O_7$ [10], $NaAlP_2O_7$ [11], or $LiFeP_2O_7$ [12] structural types. Of the few known arsenic(V) compounds of this composition, apart from compounds having $KAlP_2O_7$ and $NaAlP_2O_7$ type structures, phases having the gittinsite ($CaZrSi_2O_7$) structure were studied [13]. Most of the hitherto prepared $ABSb_2O_7$ compounds have the weberite (Na_2MgAlF_7) structure [14]. Weberite compounds are also formed in systems of pentavalent vanadium and tantalum. Cubic pyrochlore compounds were found in these systems and in niobium systems, too. Analysis of available information on $A^+B^{+3}X_2^{+5}O_7$ compounds indicates that new compounds can be prepared, especially for X = V, As, Nb, Sb, or Ta.

Our goal was to predict hitherto unprepared compounds of the title composition.

THEORY

Few attempts [15–17] to find correlations between the crystal structure type of an $A^+B^{+3}X_2^{+5}O_7$ compound and the parameters of its components concerned mainly weberite and pyrochlore compounds. As a rule, the criteria included the ratio of ionic radii of cations A^+ and B^{3+} [15, 16] and the electronegativities of elements A and B [15] (or a function of electronegativity, referred to as a relative bond ionicity [16, 17]). Lopatin et al. [15] concerned only $AgLnSb_2O_7$ compounds. Sych et al. [16] analyzed information on simpler compounds $A_2X_2O_7$, apart from $ALnX_2O_7$ weberites, pyrochlores, fluorites, and perovskites, Cai and Nino [17] tried to find classification criteria to discriminate between oxide and fluoride compounds of different compositions with weberite and pyrochlore structures. To our knowledge, there are no publications on the regularities that enable one to predict whether $A^+B^{+3}X_2^{+5}O_7$ compounds will have the $KAlP_2O_7$, $NaAlP_2O_7$, or $LiFeP_2O_7$ structure. Size factors and the electronegativities of constituent chemical elements alone do not enable one to discriminate quite accurately between the aforementioned compounds having different crystal structure types, as written in [15], too. In analysis of the projections of the points that correspond to $A^+B^{+3}X_2^{+5}O_7$ compounds having different structures onto the plane whose coordinates are the parameters proposed by Lopatin et al. [15], namely, the ratio of Shannon ionic radii for elements A and X and the Allred–Rochow electronegativity of

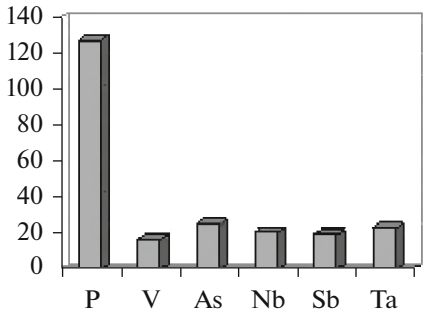

Fig. 1. Abundance bar diagram for ABX_2O_7 ($X = P^{5+}$, V^{5+}, As^{5+}, Nb^{5+}, Sb^{5+}, or Ta^{5+}) compounds.

element A, a significant overlap of the stability regions of different structural types is observed. When the electronegativity of element X is used, it is likewise impossible to discriminate between compounds with different structures. A likely reason for failure lies in that both the ionic radii and the electronegativities are important but yet not the only decisive factors for the crystal structure type of the compounds that are the subject matter of our study. One way to demarcate the stability regions of different structure types is to use the widest range of properties of components (chemical elements and binary oxides) and functions of these properties in forming the classification criteria. We propose to use precedent-based pattern recognition methods for finding such multidimensional criteria; these methods have been helpful in finding complex classification rules and in predicting (with a rather high accuracy) the probability of existence and the crystal structure type for halide compounds of various compositions [18–20].

CALCULATION METHODS

For finding multidinensional criteria that would make it possible to demarcate the stability regions of different structural types in ABX_2O_7 compounds, we used our developed information-analytical system (IAS) [21]. This system integrates a set of databases on the properties of inorganic substances and materials and a data analysis subsystem involving precedent-based pattern recognition software. The procedure for using the IAS to search over chemical information for complex regularities, to predict new inorganic compounds, and evaluate their properties is described in detail in [20]. This procedure comprises the steps of:

(1) Selecting examples for computer analysis.

(2) Selecting the initial set of properties of components (elements and binary oxides) for forming the desired criteria.

(3) Finding the component properties or simple algebraic functions of these properties that would provide for the best discrimination between different classes of compounds of the title composition.

(4) Computer-assisted analysis of the selected data with a further selection of the best discriminative criteria of those formed.

(5) Use of the found multidimensional criteria for predicting hitherto unprepared compounds.

These steps will be described in more detail.

(1) The major source of the initial data set for computer analysis was the PHASES database [9, 21] integrated into the IAS. In the examination assessment of data, a substantial problem was the assignment of crystal structures to one of the monoclinic structure types, namely, $KAlP_2O_7$, $NaAlP_2O_7$, or $LiFeP_2O_7$, for which publications often indicated the same space groups but did not give structures types, nor detailed information about the crystal structure. Polymorphism in $A^+B^{+3}X_2^{+5}O_7$ compounds also contributed to the difficulty of selecting examples for computer-assisted analysis (the sample to be analyzed was to comprise only crystal structure types at ambient temperature and pressure), since not all publications indicated the temperature and pressure at which polymorphs existed. The procedure described in [22] was used to partially automate the recognition of compounds for which an incorrect class was indicated. One problem that greatly reduces the prediction accuracy is the extremely scarce information on ABX_2O_7 compounds where X = V, As, Nb, Sb, or Ta. The total number of such compounds that have been prepared is less than the number of known phosphorus compounds (Fig. 1).

(2) Information concerning compounds was presented in the computer memory in the form of a matrix where rows included the set of parameter values for a component of some certain compound with the indication of the class to which the compound belongs. The selection of the initial component properties took into account the physical and chemical nature of the studied substances. Information concerning the properties of elements was taken from the ELEMENTS database (http://phases.imet-db.ru/elements), and information concerning oxides, from the database on the properties of binary oxides integrated into the IAS. The result of the first two steps was a computer analysis sample (a training sample).

(3) The procedure for selecting the component properties that are most important for classification from the IAS is automated, for which the IAS has special programs [23]. Previous experience in the search for criteria [15–17], which widely used algebraic functions of parameters of elements, was taken into account. Therefore, an analysis of the training sample involved the evaluation not only of the initial component properties but also of the automatically generated algebraic functions of these properties, and this greatly simplifies the subsequent formation of the desired criteria. We should mention that, even though the generation of functions is carried out using a set of elemen-

tary algebraic operations over values of the component properties that are alike in their physical meaning and dimension, the number of parameters thus formed often exceeds several hundred and even several thousands. Therefore, confining the selection of algebraic functions to be subsequently included in the desired criterion to those functions that are most important for classification will significantly speed up the construction of the criterion and often adds to the prediction accuracy. The operation of the program resulted in finding the set of parameters of the components that discriminate the set classes to the greatest extent.

(4) A set of 15 precedent-based pattern recognition programs integrated into the IAS [21] was used to search the criteria for ABX_2O_7 compound formation and the criteria that would enable one to predict the crystal structure types of these compounds under the standard ambient temperature and pressure. The prediction power of the thus-formed criteria was assessed using the cross-validation procedure, which is widely used for these purposes; for the details of this procedure, see [18, 24]. The most accurate pattern recognition algorithms were thus selected. For generating a generalized criterion that uses the merits of various algorithms, the collective decision-making procedure based on special programs [21, 24] integrated into the IAS was used. The accuracy of the criteria obtained with the use of these programs was assessed using examination recognition for 50 compounds the data on which were randomly selected from training samples and were not used in computer training (at the final prediction stage, these control examples were returned to the analysis set).

The generation of criteria included fulfilling three problems. The first of them (problem 1) comprised the search for a discrimination criterion between A_2O–B_2O_3–X_2O_5 systems where an ABX_2O_7 compound is formed and those where this compound is not formed. The second problem comprised the search for formation criteria for compounds of the indicated composition with most abundant crystal structure types ($KAlP_2O_7$, weberite, $NaAlP_2O_7$, $LiFeP_2O_7$, or pyrochlore). This problem was divided into two smaller ones. The solution of the first of them comprised the multi-class prediction of the belonging of compounds to one of the seven classes: (1) compounds with the $KAlP_2O_7$ structure, (2) weberites, (3) compounds with the $NaAlP_2O_7$ structure, (4) compounds with the $LiFeP_2O_7$ structure, (5) pyrochlores, (6) compounds with the structure differing from all above structures, and (7) systems without ABX_2O_7 compounds (problem 2). Afterwards, three problems (problems 3) were to be solved for the most abundant target classes: $KAlP_2O_7$, $NaAlP_2O_7$, and weberite in order to consecutively divide the oxide systems into three classes, where, for example, target class 1 is comprised of $KAlP_2O_7$, class 2 is comprised of compounds with the structure differing from $KAlP_2O_7$, and class 3 is comprised of the nonexistence of ABX_2O_7 compounds in A_2O–B_2O_3–X_2O_5 systems. The sets of component properties and pattern recognition algorithms were varied in solving the problems. Thus, the most discriminating set of component parameters and the most accurate (as judged from the results of cross-validation) precedent-based pattern recognition algorithms were chosen.

(5) Only component properties were used for the prediction of new compounds. All predictions were for the atmospheric pressure and room temperature. The prediction procedure and constitution of the prediction table occur in the IAS automatically. The user only enters the sets of component symbols. The final decision about the class to which the predicted compound will belong was taken on the basis of a comparison of the predictions resulting from solving all problems. If the results were mutually inconsistent, the prediction was regarded to be uncertain.

COMPUTATIONS

The computer analysis set after the examination assessment comprised data on 60 $A^+B^{+3}X_2^{+5}O_7$ compounds with the $KAlP_2O_7$ structure, 22 compounds with the weberite structure, 17 compounds with the $NaAlP_2O_7$ structure, 9 compounds with the $LiFeP_2O_7$ structure, 8 compounds with the pyrochlore structure, 72 compounds with structures differing from those above, and 12 A_2O–B_2O_3–X_2O_5 systems where ABX_2O_7 compounds are not formed. Noteworthy is a dramatic differentiation in the sizes of classes (the number of examples where compounds are formed is one order of magnitude greater than the number of examples of nonexistence of compounds). Naturally, this asymmetry can result in lower prediction accuracy, namely, for systems where compounds of the aforementioned composition are not formed.

The initial component parameter set comprised the following properties of chemical elements A, B, X, and O: pseudo-potential radius (Zunger); ionic radius (Shannon) (S15); distance from the core (S6) and valence electrons (Schubert); energies of ionization of the first, second, and third electrons (E5, E6, and E7); Mendeleev–Pettifor numbers (M1–M11); the quantum number (A5); electronegativity (Pauling); Miedema's chemical potential; the melting and boiling points (C1 and C2, respectively); standard entropy; standard enthalpy of atomization, thermal conductivity (I8), and molar heat capacity, etc. The set also comprised the thermal parameters of binary oxides A_2O, B_2O_3, and X_2O_5, namely, the melting (decomposition) temperature, standard entropy, standard heat of formation, isobaric heat capacity, and isobaric potential, 105 values altogether for each A–B–X–O system.

Table 1. Crystal structure type prediction for ABP_2O_7 compounds

B	A						
	Li	Na	K	Rb	Ag	Cs	Tl
Al	#L	#N	#K	#K	#N	K	#K
Sc	#L	#A	#K	K	A	K	K
V	#L	#N	#K	#K	#N	#K	K
Cr	#L	#N	#K	#K	#N	#K	#K
Mn	#L	?	K	#K	N	K	K
Fe	#L	K	#K	#K	#N	#K	#K
Ga	L	#N	#K	#K	#N	K	#K
Y	L	A	#K	#K	#A	#K	#K
In	#L	#N	#K	#K	#N	#K	#K
La	–	A	#–	–	A	#–	K
Ce	–	A	#–	–	A	–	K
Pr	–	A	–	–	A	?	K
Nd	#–	A	#–	–	A	–	K
Pm	?	A	?	K	A	K	K
Sm	–	A	?	?	A	?	K
Eu	?	#A	K	K	A	K	K
Gd	?	A	K	#K	A	#K	K
Tb	?	A	#A	#K	A	#K	K
Dy	?	A	?	#K	#A	#K	#K
Ho	?	#A	?	#K	#A	#K	#K
Er	?	A	K	#K	#A	#K	#K
Tm	?	A	#K	#K	#A	#K	K
Yb	?	#A	#K	#K	#A	#K	#K
Lu	?	#A	#K	#K	#A	#K	K
Bi	L	N	–	–	N	#–	K

Hereafter: K denotes the prediction of compounds with a $KAlP_2O_7$ type structure; W denotes the prediction of weberites; N, the prediction of compounds with a $NaAlP_2O_7$ type structure; L, the prediction of compounds with a $LiFeP_2O_7$ type structure; P, the prediction of pyrochlores; A, the prediction of compounds with crystal structures differing from the above structures; "–" denotes the nonexistence of ABX_2O_7 compounds in the A_2O–B_2O_3–X_2O_5 system; "?" denotes an uncertain result. "#" denotes previously studied systems data on which were used in forming multidimensional criteria.

RESULTS AND DISCUSSION

Solving the problem of predicting whether $A^+B^{+3}X_2^{+5}O_7$ compounds will form or not, we found that the ratio of the first electron ionization energy of element B to the third electron ionization energy of oxygen [E5(B)/E7(O)] and the ratio of Mendeleev–Pettifor numbers M5(B)/M1(A) were most discriminative between the "formation of a compound" (class 1) and "nonexistence of a compound" (class 2). However, a considerable overlapping of the classes was observed for projections of the points corresponding to examples of formation and nonexistence of $A^+B^{+3}X_2^{+5}O_7$ compounds onto the plane whose coordinates are the above-mentioned functions. Therefore, the set of parameters was extended by supplementing the values of these functions with 105 values of component properties. This extended set of parameters in combination with the use of pattern recognition programs based on the support vector machine, the *k*-nearest neighbors algorithm, Fisher's linear discriminant, and neural network training algorithms with majority vote for collective decision-making, made it possible to almost discriminate between the A_2O–B_2O_3–X_2O_5 systems where an ABX_2O_7 compound is formed and those where it is not.

Our attempt to use only the most discriminative parameters [C1(X) + C2(A), S15(A)/S15(X), and A5(A)/M4(X)] found by the program of [23] likewise did not provide sufficient discrimination between compounds of different crystal structure types. The best accuracy (88%) was provided by the desired criterion comprised only of the properties of elements and the use of the collective support vectors, machine, *k*-nearest neighbors, linear machine, and neural network training algorithms with majority vote for collective decision-making.

The program [23] helped us to elucidate that the values of S15(A)/S15(X) largely determine the discrimination of the compounds with the $KAlP_2O_7$ structure from compounds of other structures and from the nonexistence of ABX_2O_7 compounds in A_2O–B_2O_3–X_2O_5 systems. When the size factors were used alone, however, no satisfactory discrimination of the compounds with the $KAlP_2O_7$ structure from other classes of compounds was achieved. The best classification (with 96% accuracy) was obtained when the desired criterion was comprised only of the initial parameters of elements and binary oxides and when the pattern recognition algorithms used were the support vector machine, *k*-nearest neighbors, and logical regularities construction algorithms with majority vote for collective decision-making.

The criterion comprising the properties of elements and oxides and the functions S6(X)/S6(A) and I8(A) × I8(B) showed the highest accuracy (98%) in discriminating the compounds with the $NaAlP_2O_7$ structure from the compounds of other structures and from the systems where the compounds of predicted composition are not formed. This criterion was generated by the programs involving the estimates calculation algorithm, Fisher's linear discriminant, *k*-nearest neighbors, support vector machine, and convex stabilizer algorithms for collective decision-making.

The criterion comprised only of the most discriminative algebraic functions [M9(X)/M1(A), M10(X)/M7(X), and S15(X)–S15(O)] found by the program [23] likewise did not give a sufficient accuracy in discriminat-

Table 2. Crystal structure type prediction for ABV_2O_7 compounds

B	A						
	Li	Na	K	Rb	Ag	Cs	Tl
Al	–	A	#A	A	A	A	P
Sc	–	P	?	?	A	A	A
Cr	–	#A	#A	#A	A	#A	A
Mn	–	A	A	A	A	A	A
Fe	#–	#A	#A	A	#A	A	A
Ga	–	A	A	A	A	A	P
Y	–	#P	?	?	A	A	?
In	–	A	A	A	A	A	P
La	P	?	A	A	A	A	A
Ce	P	W	W	A	A	A	A
Pr	P	W	W	?	A	A	A
Nd	P	#W	W	A	A	A	A
Pm	?	W	W	W	A	?	A
Sm	?	#W	W	?	A	A	A
Eu	?	W	W	W	A	?	A
Gd	P	#W	W	W	A	?	A
Tb	?	W	W	W	A	?	A
Dy	?	#W	W	W	A	?	A
Ho	?	W	W	W	A	?	A
Er	?	W	W	W	A	?	A
Tm	?	W	W	W	A	?	A
Yb	?	W	W	W	A	?	A
Lu	P	W	W	?	A	?	A
Bi	?	A	A	A	A	A	P

Table 3. Crystal structure type prediction for $ABAs_2O_7$ compounds

B	A						
	Li	Na	K	Rb	Ag	Cs	Tl
Al	#A	#N	#A	#A	N	#A	#A
Sc	#A	#A	K	#K	#A	K	#K
V	A	?	A	A	?	K	K
Cr	A		#A	A	N	#K	?
Fe	#A	#N	#A	A	#N	?	A
Ga	#A	#N	#A	A	#N	A	A
Y	A	A	?	?	A	?	?
In	A	#A	A	#A	?	A	#A

ing weberites from the compounds of other structures and from the nonexistence of ABX_2O_7 compounds. However, addition of these functions to the criterion that comprised the properties of elements and oxides improved the accuracy of examination prediction

Table 4. Crystal structure type prediction for $ABNb_2O_7$ compounds

B	A						
	Li	Na	K	Rb	Ag	Cs	Tl
Al	#–	A	A	A	A	A	P
Sc	#–	P	?	A	A	A	?
Y	?	#P	P	A	A	A	?
La	A	#A	#A	A	#A	#A	A
Ce	P	?	A	A	A	A	?
Pr	P	A	A	A	A	#A	?
Nd	#P	A	A	#A	A	#A	?
Pm	P	?	?	A	A	A	A
Sm	P	W	W	A	A	A	A
Eu	P	W	W	?	A	A	A
Gd	P	P	W	?	A	?	A
Tb	P	P	W	?	A	A	A
Dy	#P	W	W	?	A	?	A
Ho	P	W	W	?	A	?	A
Er	P	?	W	?	A	?	A
Tm	P	W	W	W	A	?	A
Yb	P	W	W	?	A	?	A
Lu	P	P	?	P	A	P	A
Bi	?	#A	A	#A	?	#A	#P

Table 5. Crystal structure type prediction for $ABSb_2O_7$ compounds

B	A		
	Na	K	Ag
Al	?	A	N
Y	W	#W	A
La	#W	#W	#A
Ce	#W	W	A
Pr	#W	W	#A
Nd	#W	W	#A
Pm	W	W	A
Sm	#W	W	#A
Eu	#W	W	A
Gd	#W	W	A
Tb	#W	W	A
Dy	#W	W	A
Ho	W	#W	A
Er	W	#W	A
Tm	W	W	A
Yb	W	#W	A
Lu	W	#W	A

Table 6. Crystal structure type prediction for $ABTa_2O_7$ compounds

B	A						
	Li	Na	K	Rb	Ag	Cs	Tl
Al	#–	A	A	A	A	A	P
La	#A	#A	#A	#A	#A	#A	A
Ce	A	A	A	A	A	A	?
Pr	A	A	A	#A	A	A	A
Nd	#A	#A	#A	#A	A	#A	?
Pm	A	P	W	A	A	A	A
Sm	A	A	#W	#A	A	A	A
Eu	P	?	W	?	A	A	A
Gd	P	#P	#W	?	A	A	A
Tb	P	P	W	W	A	A	A
Dy	P	P	#W	W	A	?	A
Ho	P	P	W	W	A	W	A
Er	P	P	W	W	A	?	A
Tm	P	P	W	W	A	W	A
Yb	P	P	W	?	A	?	A
Lu	P	P	#P	?	A	?	A
Bi	?	A	A	A	?	A	#P

Table 7. Statistics of the crystal structure types predicted for $A^+B^{+3}X_2^{+5}O_7$ compounds

Structure type	X					
	P	V	As	Nb	Sb	Ta
$KAlP_2O_7$	29	0	4	0	0	0
Weberite	0	33	0	18	17	14
$NaAlP_2O_7$	3	0	2	0	1	0
$LiFeP_2O_7$	3	0	0	0	0	0
Pyrochlore	0	11	0	20	0	18

from 92 to 98%. This criterion was formed using the collective of the support vector machine, *k*-nearest neighbors, and neural network training algorithms with majority vote for collective decision-making.

The thus-formed criteria were used to predict the possibility of formation and the structure type at ambient temperature and pressure for yet-unprepared compounds. Tables 1–6 contain a part of the results of a comparison of the predictions obtained in solving all classification problems.

The analysis of data obtained shows the following (Table 7). The largest number of new ABX_2O_7 compounds are expected in phosphorus-involving systems. Weberites are predicted in the $A_2O–B_2O_3–X_2O_5$ systems, where X = V, Nb, Sb, or Ta. Few new compounds with $NaAlP_2O_7$ structures are predicted in systems involving P_2O_5, As_2O_5, and Sb_2O_5. Three yet-unprepared ABX_2O_7 compounds are predicted to have the $LiFeP_2O_7$ structure. Pyrochlores are predicted to occur in systems involving vanadium, niobium, and tantalum. The prediction accuracy cannot be high for yet-unprepared compounds in all of the above-considered systems, except for P_2O_5 systems, in view of the fewness of known examples of such compounds. However, the precedent-based pattern recognition methods we here propose for finding multidimensional criteria that would make it possible to discriminate between different classes of inorganic compound enable one to rapidly revise the sought criteria in response to the appearance of new experimental data if these data are at variance with the previous predictions, and thereby to improve prediction accuracy.

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