ISSN 0036-0236, Russian Journal of Inorganic Chemistry, 2014, Vol. 59, No. 12, pp. 1462–1471. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © N.N. Kiselyova, A.V. Stolyarenko, V.V. Ryazanov, O.V. Sen'ko, A.A. Dokukin, V.V. Podbel'skii, 2014, published in Zhurnal Neorganicheskoi Khimii, 2014, Vol. 59, No. 12, pp. 1709–1718.

THEORETICAL INORGANIC CHEMISTRY

Prediction of New Compounds in the AHal–$BHal_3$ Systems

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

[a] *Baikov Institute of Metallurgy and Materials Science, Russian Academy of Sciences, Leninskii pr. 49, Moscow, 119991 Russia*

e-mail: kis@imet.ac.ru

[b] *Dorodnitsyn Computing Center, Russian Academy of Sciences, ul. Vavilova 40, Moscow, 119333 Russia*

[c] *National Research University "Higher School of Economics," ul. Myasnitskaya 20, Moscow, 101000 Russia*

Received March 12, 2014

Abstract—Yet-nonsynthesized compounds of the compositions A_2BHal_5, A_3BHal_6, and $ABHal_4$ in systems of mono- and trivalent metal halides were predicted, and so was the type of their crystal structure under normal conditions. The calculations were performed by precedent-based pattern recognition methods using a special system for computer design of inorganic compounds. The new compounds were predicted using only the data on the properties of constituent elements and simple halides.

DOI: 10.1134/S0036023614120109

Promises of using mono- and trivalent metal halides for producing new superionic conductors [1–3] and laser [4–6], magnetic [6], and luminescent [7, 8] materials significantly stimulate the search for and investigation of new compounds in the AHal–$BHal_3$ systems, where A and B are different metals and Hal is F, Cl, Br, or I. Our developed database of properties of inorganic substances [9, 10] contains information on more than two thousands of mono- and trivalent metal halides of various compositions; however, the AHal–$BHal_3$ systems, particularly systems of bromides and iodides, are still far from being completely studied. Therefore, theoretical methods for predicting new phases in these systems are of interest.

THEORETICAL ANALYSIS

In the search for relations between the possibility of the formation of compounds in the AHal–$BHal_3$ systems and the properties of components, as criteria for distinguishing regions of stability of various phases, the ionic radii of the cations and the anion [11] or their functions, e.g., tolerance factor $t = (r_A + r_{Hal})/\sqrt{2}(r_B + r_{Hal})$ [12], are used. Criteria including only size parameters fail to be used for predicting new halide compounds with a necessary accuracy; therefore, these criteria were supplemented with other properties of the components: the charges of the cations, the electronegativities and ionization potentials of the elements, and/or algebraic functions of these parameters [13–16]. However, using additional properties of the elements by no means always enabled to correctly divide halide systems into different classes. Figure 1 presents the projection of points representing the NaCl–BCl_3 systems with and without the formation of compounds of the composition Na_3BCl_6. As coordinates, the previously [14] proposed parameters are used: the x axis is the Batsanov electronegativity X of the element B and the y axis is the function $M = z/r$, where z is the charge of the cation B and r is its Bokii–Belov ionic radius. Obviously, there is a significant overlap between objects belonging to different classes. Note that the development of such two-dimensional criteria is quite a laborious task; therefore, we proposed [17–19] to use special computer programs based on precedent-based pattern recognition algorithms [20–22], which allow one not only to automate the process of finding criteria, but also to include any number of properties of components.

CALCULATION METHODS

To find criteria for the formation of new inorganic compounds and estimate their properties, a special information-analytical system (IAS) was developed [22], which contains a set of databases of properties of inorganic compounds, a subsystem for data analysis for finding the sought-for criteria, a subsystem for predicting new compounds, a database of the found criteria, and also a set of service programs ensuring the interaction of all the subsystems and a convenient interface for the IAS user.

The procedure for finding the criteria and prediction is performed in several steps.

1. Selection of examples for computer analysis is the least formalizable problem, on the solution of which the quality of the found criteria and the accuracy of the obtained predictions largely depend. This problem is considerably simplified by the fact that the IAS user has access to the information of the databases

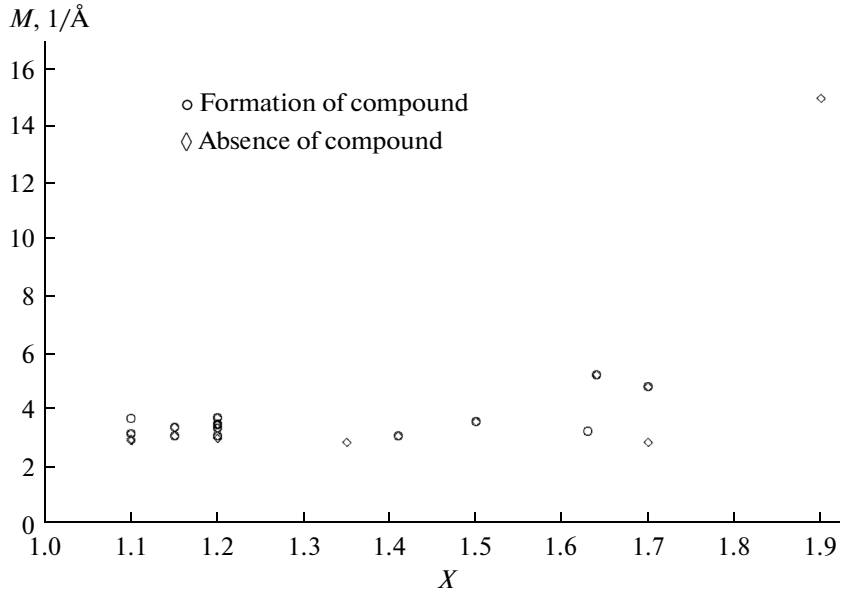

Fig. 1. Diagram of the stability regions of compounds of the composition Na_3BHal_6 in the previously proposed [14] coordinates.

of the Baikov Institute of Metallurgy and Materials Science, Russian Academy of Sciences, Moscow, Russia. These databases contain information on the properties of more than 81 thousand inorganic substances and include full texts of more than 23 thousand publications (articles, monographs, and reference books). In solving the problems of predicting new halides, the main challenge was extremely contradictory information on the existence of compounds and the type of their crystal structure under normal conditions.

2. Selection of parameters of components (chemical elements and/or simple halides) for introducing into a sought-for criterion is performed based on the physicochemical concepts of the nature of substances being studied using the database of properties of elements (http://phases.imet-db.ru/elements), the database of properties of simple halides, and a special IAS subsystem for searching the properties that are the most important for classifying substances into given classes. The search for the criteria is automated by applying a special program for generating algebraic functions using a set of elementary algebraic operations on values of parameters (uniform in physical meaning and dimension) of components of inorganic compounds being predicted. Thus, the importance for classification is estimated not only for the initial properties of components, but also for the generated functions. In addition, the visualization system included in IAS can show any projection of points to a plane, the coordinates of which is any pair of selected parameters of components or their functions, thus simplifying the understanding of the obtained results.

The output of the two steps is a matrix, or training sample, each row of which is a set of values of properties of components of an experimentally studied substance and the name of the class to which this substance belongs.

3. The data analysis subsystem of IAS currently contains 15 programs for precedent-based pattern recognition [20–22]. As a rule, it is impossible to a priori predict which of them provides the highest reliability of prediction because it is largely dependent on the specificity of the problem, the representativeness of the training sample, and the classification importance of the used parameters of components. Therefore, computer experiments are carried out for selecting the most "accurate" algorithms, which are further used for prediction. The accuracy (ratio of the number of substances for which belonging to given classes is correctly recognized to the total number of substances being recognized) was estimated using a popular procedure—examination recognition under cross-validation over training sample, which was described in detail previously [19, 20]. The output of the computer experiments is criteria for distinguishing the regions of stability of various classes of substances. Classes can be, e.g., systems with or without the formation of a compound of a given composition (problem of predicting the possibility of the formation of compounds), systems containing compounds with various types of crystal structure (problem of predicting the type of the crystal structure of compounds at given temperature and/or pressure), compounds with the melting points above or below a certain threshold value (problem of estimating properties).

4. In the vast majority of the computer experiments for selecting the most accurate pattern recognition algorithms, the best results are shown by several methods. Analysis of the results of such experiments dem-

onstrated that different algorithms often complement each other, distinguishing well the stability regions of phases over various ranges of properties of components. To obtain a consistent solution, a strategy of collectives of algorithms is widely used [20]. For this purpose, the data analysis subsystem of IAS includes a set of programs for collective decision making. However, at this step, too, the most accurate algorithm is selected, for which purpose examination recognition of 100 substances that are randomly taken from training samples and have not been used for training of computer (at the final step of predicting, control examples are returned to a sample for analysis).

The output of the last two steps is a set of the most accurate pattern recognition algorithms and collective decision making algorithm.

5. Note that the forms of the found criteria, which typically contain tens of parameters of components, are different. They may be a system of equations or inequalities, a trained neural network or growing pyramidal network, a Boolean logical expression, or a system of such expressions. Because the found criteria are often quite complex, prediction is performed by a special subsystem of IAS using only values of properties of components.

For each composition of the halides being predicted, the search for criteria and the prediction of the possibility of the formation of a substance are initially performed (problem 1), which are then followed by the search for criteria and the prediction of belonging to the most widely occurring types of crystal structure under normal conditions. The last problem is divided into two. For example, for compounds of the composition A_3BHal_6, multiclass prediction of belonging to four of the classes is made, where the four classes are cryolites, compounds with the Rb_3TlF_6 structure, compounds with the structure other than the two above, and systems containing no compounds of the composition A_3BHal_6 (problem 2). Then, the halide systems were sequentially divided into three classes, e.g., target class 1 are phases with the Rb_3TlF_6 structure, class 2 are phases with the structure other than that of Rb_3TlF_6, and class 3 is the absence of compounds of the composition A_3BHal_6 in the system A–B–Hal (problem 3). The final result of the prediction is formed by comparing the predictions made by solving all the three problems. If the results contradict each other, then the prediction is considered uncertain and the corresponding space in the prediction table is left blank.

CALCULATIONS

In this work, new mono- and trivalent metal compounds of the compositions A_2BHal_5, A_3BHal_6, and $ABHal_4$ were predicted. Computers were trained using experimental information on 101 compounds of the composition $A_2^+B^{3+}Hal_5$ (26 of which were compounds with the crystal structure of the K_2SmF_5 type (space group $Pna2_1$) under normal conditions (at room temperature and atmospheric pressure); 45, with the structure of the K_2PrCl_5 type (space group *Pnma*); 13, with the structure of the Cs_2DyCl_5 type (space group *Pbnm*); and 17, with the crystal structure other than the above) and on 174 examples of the A–B–Hal systems in which compounds of the composition A_2BHal_5 do not form; on 135 compounds of the composition $A_3^+B^{3+}Hal_6$ (38 of which were compounds with the crystal structure of cryolite (space group $P2_1/n$); 24, with the structure of the Rb_3TlF_6 type (space group $I4/mmm$); and 73, with the crystal structure other than the above) and on 105 examples of the A–B–Hal systems in which compounds of the composition A_3BHal_6 do not form; and also on 182 compounds of the composition $A^+B^{3+}Hal_4$ (13 of which were compounds with the crystal structure of scheelite (space group $I4_1/a$); 20, with the structure of the $BaSO_4$ type (space group *Pnma*); 25, with the structure of the $NaNdF_4$ type (space group $P6(-)$), 16, with the structure of the $KErF_4$ type (space group $P3_121$); 29, with the structure of the $TlTmF_4$ type (space group $P6_322$); and 79, with the crystal structure other than the above) and on 189 examples of the A–B–Hal systems in which compounds of the composition $ABHal_4$ do not form. This information was extracted from our developed database of properties of inorganic compounds (http://phases.imet-db.ru) [9, 10].

The following properties of chemical elements A, B, and Hal were taken as the input parameters: pseudopotential radius S1 (according to Zunger); ionic radius S15 (according to Shannon); distances S6 and S5 to inner and valence electrons, respectively (according to Schubert); ionization energies E5, E6, and E7 of the first, second, and third electrons, respectively; numbers (according to Mendeleev and Pettifor); number of a group in the periodic table; quantum number; number of valence electrons; electronegativity (according to Pauling); Miedema's chemical potential; melting point C1 and boiling point C2; thermal conductivity; molar specific heat I10; enthalpy of atomization; entropy I11; and so on and also thermal parameters of simple halides of the compositions AHal and $AHal_2$ (melting (decomposition) point, standard entropy S and standard values of heat of formation, specific heat at constant pressure, and potential of formation at constant pressure)—a total of 98 values for each A–B–Hal system.

RESULTS AND DISCUSSION

The calculations showed that the parameters that are the most important for classification of systems according to the criterion of the formation or absence of compounds of the composition A_2BHal_5 and according to the types of crystal structure are algebraic

Table 1. Component parameters that are the most important for classification

Property being predicted	Most important parameters of components		
	A_2BHal_5	A_3BHal_6	$ABHal_4$
Possibility of formation of compound	I11(A)*I11(Hal)	S(B)/S(A)	S1(B)*S1(Hal)
	S15(A) + S15(B)	C1(B)/C2(A)	E5(Hal) + E6(B)
Type of crystal structure	S1(A)*S1(B)	S15(A)/S15(Hal)	S1(B)*S1(Hal)
	S1(A) – S1(Hal)	S5(Hal) + S6(B)	E5(Hal) + E6(B)
	S1(A)/S1(Hal)	S(B)/S(A)	E6(Hal) + E7(B)
	S15(A) – S15(Hal)	S5(Hal) + S6(A)	S15(B)*S15(Hal)
	S15(A)*S15(B)	C2(Hal)/C1(B)	C2(A)/C1(Hal)
	E6(Hal)/E7(A)	I10(B)/I10(A)	C2(B)/C1(Hal)
		C2(A) – C1(B)	E5(B) – E6(Hal)
			E6(B) + E6(Hal)
			E6(B) + E7(Hal)

functions of properties of elements (Table 1). However, analysis of the projections of points representing substances of different classes to a plane the coordinates of which are the found algebraic functions does not allow one to conclude with sufficient confidence that the selected parameters guarantee the complete division of the given classes. Therefore, in forming classifying criteria from now on, we decided not to restrict ourselves only to the selected, most important functions, but to form three samples for describing compounds, which included the initial set of properties of elements (sample 1), the initial set of properties of elements and simple halides (sample 2), and the initial set of properties of elements and simple halides and also the computer-selected most important algebraic functions of these properties (sample 3), and use that of the samples which gives the most accurate results of the examination recognition. Such selection and use of collectives of algorithms (most often, it was a combination of algorithms: construction of logical regularities (LoReg), *k*-nearest neighbor method (KNN), training of neural network (NN), and support vector method (SVM)) enabled one to reach an average accuracy of examination recognition in solving all the three problems of above 90%. Note that, only in the search for criteria distinguishing compounds of composition being predicted with different types of crystal structures, supplementing the criteria with the selected, most informative algebraic functions of properties of elements ensured better results than using properties of elements and simple halides.

Tables 2–5 present the final results of comparing the predictions made by solving all the three classification problems for compounds of the composition A_2BHal_5. The following notation is used: (1) prediction of compounds with the crystal structure of the K_2SmF_5 type under normal conditions, (2) prediction of compounds with the structure of the K_2PrCl_5 type, (3) prediction of compounds with the structure of the Cs_2DyCl_5 type, (4) prediction of compounds with the crystal structure other than the above, and (5) prediction of the absence of compounds of the composition

Table 2. Prediction of the type of the crystal structure of compounds of the composition A_2BF_5

A / B	Li	Na	K	Rb	Ag	Cs	Tl
B	4	5	5	5	5	5	5
Al	5	#5		#5	5	5	
Sc	#5	#4	1	1	5		
Ti	5	5			5		
V	5	#5			5		
Cr	5	5			5		
Ga	5	5			5	#5	
Y	#5	#5	#1	#1	5		
In	#5				5		
Sb	5	4	4	4	5	4	4
La	#5	#5	1	#1	5	1	
Ce	#5	#5		#1	5		
Pr	#5	#5	#4	#1	5		
Nd	#5	#5	1	#1	5		
Pm	5	5	1	1	5		
Sm	#5	#5	#1	#1	5	#5	
Eu	#5	#5	#1	#1	5	1	
Gd	#5	#5	#1	#1	5	#5	
Tb	#5	#5	#1	#1	5		
Dy	#5	#5	#1	#1	5		
Ho	#5	#5	#1	#1	5		
Er	#5	#5	#1	#1	5	#5	
Tm	#5	#5	#1	#1	5		
Yb	#5	#5	#1	#1	5	#5	5
Lu	#5	#5	#1	1	5		
Bi	#5	#5	#1	1	5	1	
U	#5	#4	#4	#5	5		
Pu	#5		4		5		

Table 3. Prediction of the type of the crystal structure of compounds of the composition A_2BCl_5

B \ A	Li	Na	K	Rb	Ag	Cs	Tl
B	5	5	5	5	5	5	5
Al	#5	#5	5	5	5	#5	5
Sc	#5	#5		#5	5	#5	5
Ti	5	5			5		
V	5	5			5		
Cr	5	#5			5		
Ga	#5	#5	#5	5	#5	#5	#5
Y	#5	#5	2		#5	#3	
In	5		#4		#5		
Sb	5		#4	#5	5	#5	#5
La	#5	#5	#2	#2	#5	#2	
Ce	#5	#5	#2	#2	5	2	
Pr	#5	#5	#2	#2	5	#2	
Nd	#5	#5	#2	#2	5	2	
Pm	5	5	2	2	5	3	
Sm	5	#2	#2	#2	5		
Eu	5	#2	#2	#2	5	#3	
Gd	5	5	#2		#5	3	
Tb	5	#5	#2		5	3	
Dy	5	#5	#2	3	5	#3	
Ho	#5	#5	2	#3	5	#3	
Er	#5	#5	#5	#3	5	#3	
Tm	5	5	#4	#3	5	#3	5
Yb	5	#5		#3	#5	#3	#5
Lu	5	#5	#5	#3	5	#3	
Tl	5				5		
Bi	#5				#5		
U	5	#5	#2	#2	5	2	
Pu	#5	#5	#2	#2	5		

Table 4. Prediction of the type of the crystal structure of compounds of the composition A_2BBr_5

B \ A	Li	Na	K	Rb	Ag	Cs	Tl
B	5	5	5	5	5	5	5
Al	#5	#5	5	5	5	5	5
Sc	#5	#5	#5	#5	5	#5	5
Ti	5	5			5	5	5
V	5	5			5		5
Cr	5	5			5		
Ga	#5	#4	#5	#5	5	#5	#5
Y	5	5	5		5	5	5
In	5	4			#5		5
Sb	5			#5	5		
La	#5	#5	#2	#2	5	2	
Ce	#5	#5	#2	#2	5	2	4
Pr	5	#5	2	#2	#5	2	#4
Nd	#5	#5	#2	#2	#5	2	
Pm	5	5	2	2	5		
Sm	5	#5	#2	#2	5	2	
Eu	5	5	2	2	5	5	5
Gd	5	#5	#2	#2	5	#5	
Tb	5	#5		#5	#5	#5	#5
Dy	#5	5			5	#5	5
Ho	#5				5	#5	5
Er	5	5			5	5	5
Tm	5	#5	#5	#5	5	#5	5
Yb	5	5		#5	5	#5	5
Lu	5	5		5	5	5	5
Bi				#5	5		
U	5	#5	2	2	5		
Pu	5	5	2	2	5		

A_2BHal_5 in the A–B–Hal system. Here and hereinafter, the sign # denotes the previously studied systems the information on which was used for training of computer.

Computer analysis of information showed that the most important parameters for classification of the A–B–Hal systems according to the criterion of the formation of compounds of the composition A_3BHal_6 and according to the types of crystal structure are also functions of properties of elements and simple halides (Table 1). For example, it was demonstrated that compounds of the composition A_3BHal_6 primarily form at small values of the found functions S(B)/S(A) and C1(B)/C2(A) (Fig. 2). Supplementing the criteria with the found algebraic functions important for classification did not improve the prediction accuracy, which is clear in the context of the overlap of the stability regions, e.g., of compounds of the composition Na_3BHal_6 in the diagrams the coordinates of which are these functions (Fig. 2).

Tables 6–8 present some of the predictions of compounds of the composition A_3BHal_6 (Hal is F, Cl, or Br). The following notation is used: (1) prediction of compounds with the cryolite crystal structure under normal conditions, (2) prediction of compounds with the structure of the Rb_3TlF_6 type, (3) prediction of compounds with the crystal structure other than the above, and (4) prediction of the absence of compounds of the composition A_3BHal_6 in the A–B–Hal system.

Previously, using a program [21], we made predictions of compounds of the composition $ABHal_4$ [17]. For more than 30 years, we checked 262 compositions, and only 26 predictions disagreed with experimental data. In this work, along with the possibility of the formation of compounds, their types of crystal structure under normal conditions are predicted using additional information on new substances, a wider set of parameters of components, and collectives of algorithms.

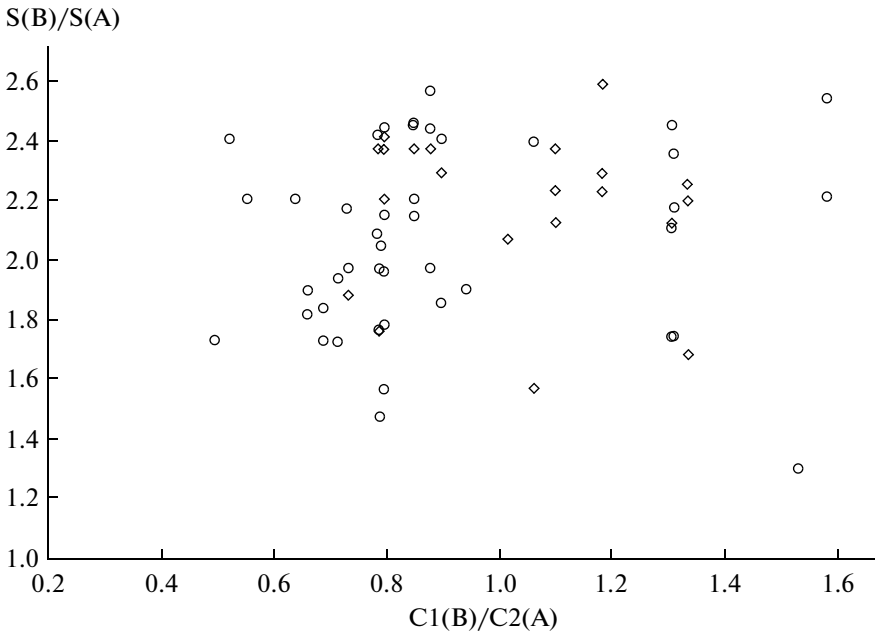

Fig. 2. Diagram of the stability regions of compounds of the composition Na_3BHal_6 in the coordinates of the functions that are the most important for classification (see notation in Fig. 1).

Much as in solving the previous problems, the results of selecting the component parameters that are the most important for classification were not the initial properties of elements or simple halides, but functions of these properties (Table 1). Tables 9–11 present some of the predictions made of compounds of the composition $ABHal_4$ (Hal is F, Cl, or Br). The following notation is used: (1) prediction of compounds with the scheelite crystal structure under normal conditions, (2) prediction of compounds with the structure of the $BaSO_4$ type, (3) prediction of compounds with the structure of the $NaNdF_4$ type, (4) prediction of compounds with the structure of the $KErF_4$ type, (5) prediction of compounds with the structure of the $TlTmF_4$ type, (6) prediction of compounds with the crystal structure other than the above, and (7) prediction of the absence of compounds of the composition $ABHal_4$ in the A–B–Hal system.

Analysis of the obtained results showed that most of the predicted compounds of the composition A_2BF_5 crystallize under normal conditions in the K_2SmF_5 structure type. For new chloride compounds of this composition, the K_2PrCl_5 and Cs_2DyCl_5 structure types are the most characteristic. The predicted compounds of the composition A_2BBr_5 and A_2BI_5 most often have the structure of the K_2PrCl_5 type. The new fluorides of the composition A_3BF_6 are characterized by the cryolite and Rb_3TlF_6 crystal structures. Most of the predicted compounds of the composition A_3BHal_6 (where Hal is Cl or Br) have the cryolite crystal structures. For the iodide compounds of this composition, the structures other than those of cryolite and Rb_3TlF_6 were predicted. Most of the predicted compounds of

Table 5. Prediction of the type of the crystal structure of compounds of the composition A_2BI_5

B \ A	Li	Na	K	Rb	Ag	Cs	Tl
B	5	5	5	5	5	5	5
Al	5	5	#5	5	5	#5	5
Sc	5	#5	#5	#5	5	#5	5
Ti	5	5	5	5	5	5	5
V	5	5	5	5	5	5	5
Cr	5	5	5	5	5	5	5
Ga	5	5	5	5	#5	5	5
Y	5	#5	#5	#5	5	#5	5
Mo	5				5		5
In	5	5		5	#5	5	#5
Sb	5			#5		5	
La	5	#5	#2	#2	5	#5	
Ce	5	5	#2	#2	5	#4	
Pr	5	#5	#2	#2	5	#4	5
Nd	5	5	#2	#2	5		5
Pm	5	5	5	5	5	5	5
Sm	#5	#5		#5	5	#5	5
Eu	5	5	5	5	5	5	5
Gd	5	#5	#5	5	5	#5	5
Tb	5	5	5	5	5	#5	5
Dy	5	5	#5	5	5	#5	5
Ho	#5	#5	#5	#5	#5	#5	#5
Er	5	#5	#5	5	5	#5	5
Tm	5	5	5	5	5	#5	5
Yb	5	5	5	5	5	5	5
Lu	5	5	5	5	5	#5	5
Bi	#5			#5	#4	#5	#4
U	5	5	2	2	5		5
Pu	5	5		2	5	5	5

Table 6. Prediction of the type of the crystal structure of compounds of the composition A_3BF_6

B \ A	Li	Na	K	Rb	Ag	Cs	Tl
B	4	#4			2		
Al	3	#1	3	3	#2	3	
Ti	3	#1			2		
V	#3	#1	3		2	#3	
Cr	3	#1	3	3	#2		
Mn	3	#1	3		2		3
Fe	3	#1	3	2	2	2	3
Co	3	#1	#3	#3	2	#3	
Ga	#3	#1		3	#2	#3	3
Y	4			#2		#2	3
Mo	3	1	#3	3	2	3	3
In	3	#1	3	#3	#1	3	
Sb			#4	#4		4	
La	#4	#4	2	2		2	
Ce	#4	#4	#3	2	1	#3	
Pr	#4	#4	#2	2		#2	
Nd	#4	#4	#2	2		#2	
Pm	4	4	1	2		2	
Sm	#4	#4	#2	2	1	#2	
Eu	#4	#4	#1	2		#2	
Gd	#4	#4	#1	#2	1	#2	
Tb	#4	#4	#1	#2	1	#2	
Dy	#4	#4	#1	#2		#2	
Ho	#4	#4	#1	2		#2	
Er	#4	#4	1	2		#2	
Tm	#4	#4	#1	#2		#2	
Yb	#4	4	#1	#2		#2	
Lu	#4	#4	1	2		#2	
Bi	#4	#4				3	
U	#4	#4	#3	#2		#2	4
Pu	#4	4	3	2	1	2	

Table 7. Prediction of the type of the crystal structure of compounds of the composition A_3BCl_6

B \ A	Li	Na	K	Rb	Ag	Cs	Tl
B	4		4		4		
Al	#4				4	#4	
P	#4	#4	4	#4	#4	#4	#4
Sc	3	#1	3	3	#3	3	3
Ti	3	#1	3	3	3	3	
V	3	#3	3	3		3	
Cr	3	#3	3	3		#3	3
Fe	3	3	3	3		3	
Ga	#4	#4	#4	4	#4	#4	#4
Y	#3	#1	3	3	3	3	
Mo	3	#3	3	3		3	
Ru	3	3	3	3		3	
Rh	3	3	3	3		3	
In	3	#3	3	3		3	#3
Sb	4				4		
La	#4	#4	#3	#3	#4	3	#4
Ce	#4	#4	#3	3	4	3	4
Pr	#4	4	#3	3	4	3	4
Nd	#4	#4	#3	3	4	3	4
Pm	3	4	3	3		3	
Sm	4	#4	3	3	3	3	
Eu	3	#3	3	3	3	3	3
Gd	3	#3	3	3	#4	3	3
Tb	#3	#3	3	3		3	3
Dy	#3	#1	1	3	#3	3	3
Ho	#3	#1	1	3	#3	3	3
Er	#3	#1	1	3	#3	3	3
Tm	#3	#1	1	2	#3	3	3
Yb	#3	#1	1	2	#3	3	3
Lu	#3	#1		3	#3	3	3
Ir	3	3	#3	3		3	
Tl	3	3	#3	#3		#3	
Bi	#4	#1	3	#3	#4	#3	
U	#4	4	3	3	4	3	4
Pu	#4	#4	3	3	4	#3	4

Table 8. Prediction of the type of the crystal structure of compounds of the composition A_3BBr_6

B \ A	Li	Na	K	Rb	Ag	Cs	Tl
B	4	4	4	4	4		4
Al	#4	#4	4	4	4	4	4
Sc	3	#3	3	3	3	3	
Ti	3		3	#3	3	#3	
V	3	3	3	3	3	3	
Cr	3	3	3	3		#3	
Fe		3	3	3	4	3	
Ga	#4		#4	#4	4	#4	#4
Y	3	1	3	3		3	
Mo	3	3	3	3		3	
Rh	3	3	3	3		3	
In	#3		#3	3	#4	3	
Sb	4			#4	4	#4	4
La	#4	#4	3	3		3	
Ce	4	#4	3	3		3	
Pr	4	#4	3	3		3	
Nd	#4	#4	3	3		3	
Pm	3	3	3	3		3	
Sm		4	3	3		3	
Eu	3	#3	3	3	3	3	3
Gd	3	#1	3	3		3	
Tb	3	1	#3	3		3	
Dy	3	1	3	3	3	3	
Ho	3	1	3	3	3	3	
Er	3	1	3	3	3	3	
Tm	3	1	3	3	3	3	3
Yb	3	1	3	3	3	3	3
Lu	3	1	3	3	3	3	
Ir	3	3	3	3		3	
Bi	#4	#4	3	3	4	#3	
U	4	#4		3		3	4
Pu		4	3	3		3	

Table 9. Prediction of the type of the crystal structure of compounds of the composition ABF_4

B \ A	Li	Na	K	Rb	Ag	Cs	Tl
B	#6	#6	#2	#2	#2	#2	#2
Al	6	6	6	6		6	#6
Sc	1	#6	#6		#4		#6
Ti		6	6	6	4	6	6
V	6	#6	6	6	4	6	6
Cr	6	#6	6	6		#6	6
Fe	6	#6	6	6			
Co	#6	6	6	6			
Ga	6	6	6	6		2	6
Y	#1	#3	#4	#5	#4	#5	#5
Mo	6	6	6	6			
In	6	#6	6	6	#4	6	#6
Sb	6	#6	6	#6		6	#6
La	#7	#3			3	5	
Ce	#7	#3			3	#5	5
Pr	#7	#3			3	#5	5
Nd	#7	#3			#3	#5	5
Pm	#7	#3		5	3	5	5
Sm	#7	#6		#5	#3	#5	5
Eu	#1	#3		#5	#3	#5	5
Gd	#1	#3		#5	#3	#5	#6
Tb	#1	#3	#4	#5	#3	#5	5
Dy	#1	#3	#4	#5	#3	#5	5
Ho	#1	#3	#4	5	#3	5	#5
Er	#1	#3	#4	#5	#4	#5	#5
Tm	#1	#6	#4	#5	#4	#5	#5
Yb	#1	#6	#4	#5	#4	#5	#5
Lu	#1	#6	#4	#5	#4	#5	#5
Bi		#6	6	#6	#3	#7	6
U	#7	#3		#4	3		
Pu	#7	#3	#3		3	5	5

the composition ABF_4 have the structures of the $NaNdF_4$, $KErF_4$, and $TlTmF_4$. The new chloride, bromide, and iodide compounds of this composition primarily crystallize in the barite structure.

By the pattern recognition methods, we found the parameters of components that determine the possibility of the formation and the type of the crystal structure of complex halides under normal conditions. In all the cases, the parameters that were the most important for classification were functions of the initial properties of components (Table 1), namely, size factors (Zunger pseudopotential radii S1 and Shannon ionic radii S15) and energy parameters (ionization energies E5, E6, and E7 of the first, second, and third electrons of atoms of elements, respectively). Much smaller contributions to the classification of complex halides were made by thermochemical parameters (specific heat I10; entropies I11 and S of elements and

Table 10. Prediction of the type of the crystal structure of compounds of the composition $ABCl_4$

B \ A	Li	Na	K	Rb	Ag	Cs	Tl
B	6	6	2	2	2	2	2
Al	#6	6	#6	#2		#2	#2
P	#7	#7	7	#7	#7	#7	#7
Sc	#7	7	#7	#7	7	#7	7
Ti	6	6					
V	6	6	6	2		2	2
Cr	6	6	6	2	6	2	2
Fe	#6	6	#6	#2	4	#2	#2
Ga	#6	6	#6	#2		#2	#2
Y	#7	7	#7	#7	#7	#7	7
Mo	6	6	6	2		2	2
Ru	6	6	6		6	2	
Rh	6	6	6		6	2	
In	6	6	6		#7		#6
Sb	6	6	6	#6	7	#7	#7
La	#7	#7	#7	#7	#7	#7	#7
Ce	#7	#7	#7	#7	7	7	7
Pr	#7	#7	#7	#7	7	#7	7
Nd	#7	#7	#7	#7	7	#7	7
Pm			7	7	7	7	7
Sm	7	#7	#7	#7	7	#7	7
Eu	7	#6	#7	#7	7	#7	7
Gd	#1	#6	#7	7	#7	#7	#7
Tb		6	#7	#7	7	7	7
Dy		#6	#7	#7	7	#7	7
Ho		#6	#7	#7	7	#7	7
Er	#7	6	#7	#7	7	#7	7
Tm		#6	#7	#7	7	#7	7
Yb	#7	6	#7	#7	7	#7	#7
Lu		6	#7	7	7	7	7
Ta	6	6		2		2	2
Ir	6	6				2	
Bi	6	6	6				
U	#7	#7	#7		7	#6	7
Pu	#7	#7	#7	#7	7	#7	7

Table 11. Prediction of the type of the crystal structure of compounds of the composition $ABBr_4$

B \ A	Li	Na	K	Rb	Ag	Cs	Tl
B				2		2	
Al	6	6	#6	#2	6	#2	#6
Sc	7	#7	#7	#7	7	#7	
Ti	7	7			7		7
V	6	6	6	2	6	2	
Cr	6	6	6	2	6	2	
Fe	#6	6	6	#2	#6	#2	
Ga	#6	6	#6	#2	6	#2	#6
Y	7	7	7	7	7	7	7
Mo	6	6	6	2	6	2	
Rh	6	6	6		6	2	6
In	7	6	6		7	#7	6
Sb			#7	#7	7	#7	7
La	#7	#7	#7	#7	7	#7	
Ce	#7	#7	#7	#7	7	#7	
Pr	7	#7	#7	#7	#7	7	
Nd	#7	#7	#7	#7	#7	7	
Pm	7	7	7	7	7	7	
Sm	7	#7	#7	#7	7	#7	
Eu	7	7	7	7	7	7	
Gd	7	#7	#7	#7	7	#7	
Tb	7	#7	#7	#7	#7	#7	#7
Dy	#7	7	#7	#7	7	#7	
Ho	#7	#7	7	7	7	#7	
Er	7	7	#7	#7	7	7	
Tm	7	#7	#7	#7	7	#7	
Yb	7	7	#7	#7	7	#7	
Lu	7	7	7	7	7	7	
Bi	#7	#7	7	#7	7	7	7
U	7	#7	#7	#7	7	#7	
Pu	7	7	7	7	7	7	

simple halides in the solid state, respectively; and melting points C1 and boiling points C2 of elements) and electron factors (Schubert distances S6 and S5 to core and valence electrons, respectively).

Using the precedent-based pattern recognition methods enabled us to automate the search for criteria of the formation of inorganic compounds with given properties, including criteria involving any number of parameters of components. The IAS developed for designing inorganic compounds provides chemists with a wide range of databases containing information on tens of thousands of substances and with software including programs for analyzing data to find sought-for criteria, visualizing obtained results, and predicting new compounds. The proposed approach to solv-

ing the problems of predicting new inorganic compounds and the developed algorithms and software allowed us to predict new phases in halide systems with high accuracy.

ACKNOWLEDGMENTS

We thank L. D. Rozhnov and V. A. Dudarev for their help in developing programs.

This work was supported in part by the Russian Foundation for Basic Research (project nos. 11-07-00715, 12-07-00142, and 14-07-00819).

REFERENCES

1. A. Bohnsack, F. Stenzel, A. Zajonc, et al., Z. Anorg. Allgem. Chem. **623**, 1067 (1997).
2. A. Bohnsack, G. Balzer, M. S. Wickleder, et al., Z. Anorg. Allgem. Chem. **623**, 1352 (1997).
3. K. Lerch, W. Laqua, and G. Meyer, Z. Anorg. Allgem. Chem. **582**, 143 (1990).
4. M. Haase and H. Schäfer, Angew. Chem., Int. Ed. Engl. **50**, 5808 (2011).
5. L. Cheng, C. Wang, and Z. Liu, Nanoscale **5**, 23 (2013).
6. Z. Yi, G. Ren, L. Rao, et al., J. Alloys Compd. **589**, 502 (2014).
7. M. A. Gusowski, A. Gagor, M. Trzebiatowska-Gusowska, and W. Ryba-Romanowski, J. Solid State Chem. **179**, 3145 (2006).
8. A. K. Tyagi, J. Kohler, P. Balog, and J. Weber, J. Solid State Chem. **178**, 2620 (2005).
9. E. M. Savitskii, N. N. Kiseleva, B. N. Pishchik, et al., Dokl. Akad. Nauk SSSR **279** (3), 627 (1984).
10. N. Kiseleva, D. Murat, A. Stolyarenko, et al., Inform. Resursy Ross., No. 4, 21 (2006).
11. J. M. Haschke, *Handbook on the Physics and Chemistry of Rare Earths*, Ed. by K. A. Gschneidner, Jr., and L. Eyring (North-Holland, Amsterdam, 1979), Vol. 4, p. 89.
12. R. E. Thoma, Inorg. Chem. **1**, 220 (1962).
13. P. P. Fedorov and P. I. Fedorov, Zh. Neorg. Khim. **18**, 205 (1973).
14. A. G. Dudareva, A. K. Molodkin, and G. A. Lovetskaya, Zh. Neorg. Khim. **33**, 1613 (1988).
15. K. B. Dzeranova, Izv. Ros. Gos. Ped. Univ. Im. A.I. Gertsena **4** (8), 94 (2004).
16. V. N. Chikanov, Russ. J. Inorg. Chem. **54**, 1099 (2009).
17. N. N. Kiseleva and E. M. Savitskii, Zh. Neorg. Khim. **27**, 2880 (1982).
18. N. N. Kiseleva and E. M. Savitskii, Zh. Neorg. Khim. **29**, 3104 (1984).
19. N. N. Kiseleva, Russ. J. Inorg. Chem. **59**, 496 (2014).
20. Yu. I. Zhuravlev, V. V. Ryazanov, and O. V. Sen'ko, *"RASPOZNAVANIE". Mathematical Methods. Program System. Practical Applications* (FAZIS, Moscow, 2006) [in Russian].
21. V. P. Gladun, *Processes of Formation of New Knowledge* (Pedagog 6, Sofia, 1995) [in Russian].
22. N. N. Kiselyova, A. V. Stolyarenko, V. V. Ryazanov, et al., Pattern Recogn. Image Anal. **21**, 88 (2011).

Translated by V. Glyanchenko