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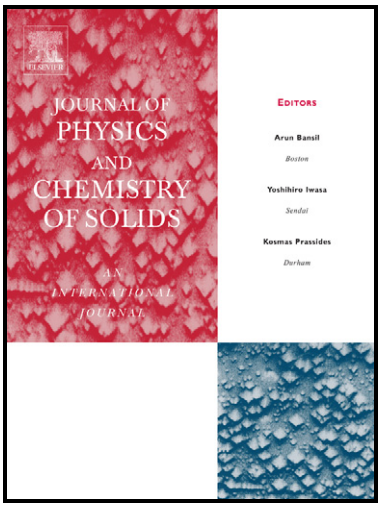

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Modeling of lattice constant and their relations with ionic radii and electronegativity of constituting ions of A_2XY_6 cubic crystals (A=K, Cs, Rb, Tl; X=tetravalent cation, Y=F, Cl, Br, I)

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Abstract

In the present paper a new empirical model is proposed to describe and predict the lattice constants for a series of cubic crystals, all of which have the A_2XY_6 composition (A = K, Cs, Rb, Tl; X = tetravalent cation, Y = F, Cl, Br, I). The model is based on a thorough analysis of structural properties of 85 representative crystals from this group. It was shown that the lattice constant is a linear function of the ionic radii and electronegativity of the constituting ions. A simple empirical equation was obtained as a result of the performed analysis. It gives very good agreement between the experimental and modeled values of the lattice parameters, with an average error not exceeding 1.05 %. The developed approach can be efficiently used for a simple, fast and reliable prediction of lattice constants and interionic distances in isostructural materials having a similar composition.

Keywords

A. Inorganic compounds, D. Crystal structure

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1. Introduction

A unique description of any crystal structure can be provided by the set of the crystal lattice parameters and atomic (ionic) positions. Experimentally, the values of the crystal lattice parameters can be precisely determined using the X-ray diffraction technique. Theoretically, thanks to very rapid development of reliable *ab initio* methods of calculations, the crystal lattice parameters can be computed from the first principles, and the difference between the theoretical and experimental lattice parameters for the same crystal typically does not exceed a few percents on average.

However, it can be noted that the experimental techniques used for determination of the crystal lattice parameters require special sophisticated equipment; and the *ab initio* methods of crystal structure calculations are time-consuming. In this connection, reliable methods of a quick estimation of the crystal lattice parameters based on simple empirical rules would be useful for further research in this field. Such methods may be very helpful for prediction of the lattice constants (LC) of newly synthesized materials. Moreover, such methods can help in choosing proper substrates for the growth of thin films or in selecting suitable chemical elements as potential candidates for new compounds.

It has been recognized for a long time already that the ionic radii, electronegativity, and oxidation state are crucial physical parameters, which determine the LC values [1]. A thorough analysis of a large number of reliable experimental structural data allows for finding and highlighting certain trends linking together the above-mentioned parameters.

Cubic crystals with their single crystal lattice parameter *a* are of particular interest for empirical analysis of relationship between the LC and properties of particular chemical elements. Recently, several works [2–6] were published, which dealt with empirical modeling of the LC for the perovskite crystals. The linear relations between the value of *a* and several other variables (ionic radii, number of valence electrons, and electronegativity) in several different combinations were proposed and successfully tested.

In the present work another class of cubic crystals – the A_2XY_6 compounds (A = K, Cs, Rb, Tl; X = tetravalent cation, Y = F, Cl, Br, I) – is considered with an aim of finding empirical rules allowing to describe the LC of already existing compounds and predict the LC of those new materials from this group, which can be in principle synthesized.

The members of the considered group of compounds have been subjected to thorough investigations, both experimental and theoretical [7–10 etc], since they can be easily doped with different impurity ions (especially at the 6-fold coordinated tetravalent cation site), thus offering a good opportunity to study the crystal field effects in the octahedral coordination.

The experimental structural data on 85 representatives of the A_2XY_6 group (which can be categorized into four subgroups depending on the halogen ions: 17 fluorides, 41 chlorides, 18 bromides, and 9 iodides) have been used in the present paper to derive an empirical equation, which

describes the overall trend for the lattice constant in this series of compounds and can be used for a predictive estimation of the LC of new similar crystals.

2. Results and discussion

The chosen crystals possess Fm-3m space group, with four formula units in one unit cell. In this structure each monovalent cation A is 12-fold, and each tetravalent cation X is 6-fold coordinated (both by the halogen ions). Each anion Y is 6-fold coordinated. One unit cell of this crystal structure is shown in Fig. 1.

Fig. 1.

In this structure, the A cation coordinates (in the unit of the lattice constant) are (0.25, 0.25, 0.25), the X cation coordinates are (0, 0, 0), and the halogen ion coordinates are (x, 0, 0), where x is somewhat different (varying around 0.2) for different structures. Following the structure and existing equivalent positions, the doubled A – A distance is equal to the LC. Two other simple relations between the LC and inter-ionic distances are depicted in Fig. 2: a = 1.416 d(X–X) and a = 2.30916 d(A–X) (in these equations all distances are in Å). In addition, it is easy to get from the geometrical consideration that d(Y–Y) = $\sqrt{2}$ d(X–Y).

In these crystals the upper valence band is formed by the p states of halogen ions and the bottom of conduction bands is formed prevailingly by the cationic s states. The nature of the chemical bonds is mainly derived from the Coulomb interactions between the particular ions. So it is possible to conclude then that the electronegativity and ionic radii may be crucial for the formation of the stable structure, the lattice parameters of which are determined by the competition between the ionic Coulomb and exchange correlation contributions. The principal role here is played by the charge transfer of the electronic clouds and the hybridization of the corresponding orbitals. Usually incorporation of the d-transition metal ions (in the case of doped crystals) gives additional localized d-states, which form the bottom of the conduction bands.

Fig. 2.

Table 1 contains the LC, ionic radii [11] and electronegativity [12] values of all elements, which appear in the considered compounds. A quick glance at the data gathered in the Table shows that the LC values increase with increasing halogen's ion atomic number, i.e. in the F → Cl → Br → I direction; the smallest values of a is 8.109 Å for K_2NiF_6, and the largest value is 11.620 Å for Rb_2SnI_6.

The shortest and longest inter-ionic distances are as follows: the A – Y distance varies from 2.878 Å in K_2NiF_6 to 4.109 Å in Rb_2SnI_6; the X – Y distance is in the range from 1.677 Å in K_2SiF_6 to 2.847 Å in Rb_2SnI_6; the A – X distance changes from 3.511 Å in K_2NiF_6 to 5.032 Å in Rb_2SnI_6.

Table 1.

Although the ionic radii represent a most crucial factor governing the crystal lattice structure and its parameters, the ionic radii alone cannot describe properly the LC variation in this series. A good example can be taken from Table 1: the LC values for Cs_2GeF_6 and Cs_2MnF_6 are slightly different, whereas the ionic radii of Ge^{4+} and Mn^{4+} ions – the only different ions in these crystals – are equal. To handle properly this and similar situations, electronegativity of corresponding chemical elements should be also considered.

Because the LC represents a balance between the effective ionic radii and their electronegativity, the LC in the proposed model was expressed as a linear function of the following variables: two sums of ionic radii ($R_A + R_X$), ($R_X + R_Y$), and difference of electronegativities $(\chi_Y - \chi_X)$. The least square fit resulted in the following linear function, describing the LC of the chosen crystals (all distances are expressed in Å):

$$a = 1.96325(R_A + R_X) + 0.98102(R_X + R_Y) + 0.07593(\chi_Y - \chi_X) + 0.57901 \quad (1)$$

Fig. 3.

The correlation between the experimental and predicted by Eq. (1) LC is presented in Fig. 3. The numerical results obtained by using Eq. (1) are also given in Table 1. In spite of a very simple form of Eq. (1), it gives a very good estimate of the lattice parameters. The maximum error between the experimental and predicted LC is 4.39 % for K_2HfF_6. The average error is 1.05 %; the root-mean-squared deviation between the calculated and experimental LC is 0.137 Å. Inclusion of the electronegativities of the A ions as an additional variable does not lead to any improvement of the fit quality.

Analysis of data from Table 1 shows that out of 85 considered compounds, for 55 the error is less than 1 %, for 21 this error is between 1 % and 2 %, and only for 9 of them the relative error exceeds 2 %, which proves application of Eq. (1) to the analysis and modeling of the LC for the considered crystals.

Following the developed model, one can expect that this approach concerning optical and electronic properties may be extended as well to the layered crystals [70, 71], for which the anisotropy of the chemical bonds is closely related to the anisotropy of the corresponding optical and electronic properties.

3. Conclusions

The modeling of the crystal lattice parameters for 85 considered A_2XY_6 cubic compounds performed in the present work allowed to establish a simple empirical linear relationship between the lattice constant, ionic radii and electronegativities for the constituting ions. Agreement between the experimental and predicted lattice constants is good, with an average error of 1.05 % only. Such a value of the average error is comparable with the differences (usually not exceeding 1-3 %) between the experimental lattice constants and the corresponding values calculated by using the *ab initio* methods. The obtained empirical dependence of the lattice constant on the sum of ionic radii and electronegativity difference, expressed by Eq. (1), can be effectively used by the materials scientists working with these crystalline materials since it gives an opportunity to apply a very simple, reliable and efficient relation to evaluate the lattice constants and inter-ionic distances for new materials of the considered group of crystals.

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Table 1. Experimental data on lattice constants, ionic radii and electronegativity for 85 A_2XY_6 compounds, in comparison with predicted lattice constants, based on the proposed model. Coordination numbers of the A, X, Y ions are given in the parenthesis.

	Lattice constant, experiment, Å	Ionic radii, Å [11]			Electronegativity [12]			Lattice constant, predicted	Difference, (exp.-predict.), Å	Error, %
		$R_A(12)$	$R_X(6)$	$R_Y(6)$	χ_A	χ_X	χ_Y			
Cs_2GeF_6	8.990 [13]	1.88	0.53	1.33	0.79	2.01	3.98	8.855	0.135	1.50
Cs_2MnF_6	8.972 [14]	1.88	0.53	1.33	0.79	1.55	3.98	8.890	0.082	0.91
Cs_2NiF_6	8.938 [15]	1.88	0.48	1.33	0.79	1.91	3.98	8.814	0.124	1.39
Cs_2PdF_6	9.000 [16]	1.88	0.615	1.33	0.79	2.2	3.98	8.924	0.076	0.84
Cs_2PtF_6	9.050 [17]	1.88	0.625	1.33	0.79	2.2	3.98	8.934	0.116	1.28
Cs_2SiF_6	8.890 [18]	1.88	0.40	1.33	0.79	1.9	3.98	8.736	0.154	1.73
Rb_2CrF_6	8.523 [15]	1.72	0.55	1.33	0.82	1.66	3.98	8.587	-0.064	0.76
Rb_2GeF_6	8.5825 [19]	1.72	0.53	1.33	0.82	2.01	3.98	8.541	0.041	0.48
K_2HfF_6	9.010 [20]	1.64	0.71	1.33	0.82	1.3	3.98	8.615	0.395	4.39
K_2MnF_6	8.221 [14]	1.64	0.53	1.33	0.82	1.55	3.98	8.419	-0.198	2.41
K_2NiF_6	8.109 [21]	1.64	0.48	1.33	0.82	1.91	3.98	8.343	-0.234	2.88
K_2SiF_6	8.1419 [22]	1.64	0.40	1.33	0.82	1.90	3.98	8.265	-0.123	1.51
Rb_2MnF_6	8.531 [14]	1.72	0.53	1.33	0.82	1.55	3.98	8.576	-0.045	0.53
Rb_2NiF_6	8.462 [15]	1.72	0.48	1.33	0.82	1.91	3.98	8.500	-0.038	0.45
Rb_2PdF_6	8.570 [16]	1.72	0.615	1.33	0.82	2.2	3.98	8.610	-0.040	0.47
Rb_2SiF_6	8.446 [23]	1.72	0.40	1.33	0.82	1.90	3.98	8.422	0.024	0.28
Tl_2SiF_6	8.580 [23]	1.70	0.40	1.33	1.8	1.90	3.98	8.383	0.197	2.30
Cs_2GeCl_6	10.230 [24]	1.88	0.53	1.81	0.79	2.01	3.16	10.206	0.024	0.23
Cs_2IrCl_6	10.2119 [25]	1.88	0.625	1.81	0.79	2.2	3.16	10.285	-0.073	0.72
Cs_2MoCl_6	10.2121 [26]	1.88	0.65	1.81	0.79	2.16	3.16	10.313	-0.101	0.98
Cs_2PbCl_6	10.416 [27]	1.88	0.775	1.81	0.79	1.8	3.16	10.463	-0.047	0.45
Cs_2PtCl_6	10.192 [27]	1.88	0.625	1.81	0.79	2.2	3.16	10.285	-0.093	0.91
Cs_2ReCl_6	10.255 [28]	1.88	0.63	1.81	0.79	1.9	3.16	10.313	-0.058	0.56
Cs_2SeCl_6	10.260 [27]	1.88	0.50	1.81	0.79	2.55	3.16	10.136	0.124	1.21
Cs_2SnCl_6	10.3552 [29]	1.88	0.69	1.81	0.79	1.96	3.16	10.367	-0.012	0.11
Cs_2TaCl_6	10.271 [30]	1.88	0.68	1.81	0.79	1.5	3.16	10.392	-0.121	1.18
Cs_2TeCl_6	10.445 [27]	1.88	0.97	1.81	0.79	2.1	3.16	10.631	-0.186	1.78
Cs_2TiCl_6	10.219 [27]	1.88	0.61	1.81	0.79	1.54	3.16	10.320	-0.101	0.99
Cs_2WCl_6	10.245 [31]	1.88	0.66	1.81	0.79	1.7	3.16	10.357	-0.112	1.10
Cs_2ZrCl_6	10.428 [27]	1.88	0.72	1.81	0.79	1.33	3.16	10.444	-0.016	0.16
K_2MnCl_6	9.6445 [32]	1.64	0.53	1.81	0.82	1.55	3.16	9.770	-0.126	1.30
K_2MoCl_6	9.850 [33]	1.64	0.65	1.81	0.82	2.16	3.16	9.841	0.009	0.09
K_2OsCl_6	9.729 [34]	1.64	0.63	1.81	0.82	2.2	3.16	9.819	-0.090	0.92
K_2PdCl_6	9.7097 [35]	1.64	0.615	1.81	0.82	2.2	3.16	9.804	-0.094	0.97
K_2PtCl_6	9.751 [36]	1.64	0.625	1.81	0.82	2.2	3.16	9.814	-0.063	0.64

K_2ReCl_6	9.840 [37]	1.64	0.63	1.81	0.82	1.9	3.16	9.842	-0.002	0.02
K_2RuCl_6	9.737 [38]	1.64	0.62	1.81	0.82	2.2	3.16	9.809	-0.072	0.74
K_2SnCl_6	9.9877 [39]	1.64	0.69	1.81	0.82	1.96	3.16	9.896	0.092	0.92
K_2TaCl_6	9.9935 [40]	1.64	0.68	1.81	0.82	1.5	3.16	9.921	0.073	0.73
K_2TcCl_6	9.830 [41]	1.64	0.645	1.81	0.82	2.1	3.16	9.841	-0.011	0.11
K_2TiCl_6	9.792 [42]	1.64	0.61	1.81	0.82	1.54	3.16	9.849	-0.057	0.58
K_2WCl_6	9.8223 [43]	1.64	0.66	1.81	0.82	1.7	3.16	9.886	-0.064	0.65
Rb_2MnCl_6	9.838 [44]	1.72	0.53	1.81	0.82	1.55	3.16	9.927	-0.089	0.91
Tl_2MoCl_6	9.8635 [45]	1.70	0.65	1.81	1.8	2.16	3.16	9.959	-0.096	0.97
Rb_2NbCl_6	9.989 [46]	1.72	0.68	1.81	0.82	1.6	3.16	10.070	-0.081	0.82
Rb_2PbCl_6	10.195 [27]	1.72	0.775	1.81	0.82	1.8	3.16	10.148	0.047	0.46
Rb_2PdCl_6	9.990 [47]	1.72	0.615	1.81	0.82	2.2	3.16	9.961	0.029	0.29
Rb_2PtCl_6	9.884 [27]	1.72	0.625	1.81	0.82	2.2	3.16	9.971	-0.087	0.88
Tl_2PtCl_6	9.755 [27]	1.70	0.625	1.81	1.8	2.2	3.16	9.932	-0.177	1.81
Rb_2SeCl_6	9.978 [27]	1.72	0.50	1.81	0.82	2.55	3.16	9.822	0.156	1.57
Rb_2SnCl_6	10.137 [48]	1.72	0.69	1.81	0.82	1.96	3.16	10.053	0.084	0.83
Rb_2TeCl_6	10.233 [49]	1.72	0.97	1.81	0.82	2.1	3.16	10.317	-0.084	0.82
Rb_2TiCl_6	9.922 [27]	1.72	0.61	1.81	0.82	1.54	3.16	10.006	-0.084	0.85
Rb_2WCl_6	9.957 [50]	1.72	0.66	1.81	0.82	1.7	3.16	10.043	-0.086	0.87
Rb_2ZrCl_6	10.178 [27]	1.72	0.72	1.81	0.82	1.33	3.16	10.130	0.048	0.47
Tl_2SnCl_6	9.970 [27]	1.70	0.69	1.81	1.8	1.96	3.16	10.014	-0.044	0.44
Tl_2TeCl_6	10.107 [27]	1.70	0.97	1.81	1.8	2.1	3.16	10.278	-0.171	1.69
Tl_2WCl_6	9.8873 [31]	1.70	0.66	1.81	1.8	1.7	3.16	10.004	-0.117	1.18
Cs_2NpBr_6	11.082 [52]	1.88	0.87	1.96	0.79	1.3	2.96	11.020	0.062	0.56
Cs_2PoBr_6	10.990 [53]	1.88	0.94	1.96	0.79	2.0	2.96	11.036	-0.046	0.42
Cs_2PtBr_6	10.670 [54]	1.88	0.625	1.96	0.79	2.2	2.96	10.712	-0.042	0.39
Cs_2SnBr_6	10.770 [55]	1.88	0.69	1.96	0.79	1.96	2.96	10.794	-0.024	0.22
Cs_2TeBr_6	10.873 [48]	1.88	0.97	1.96	0.79	2.1	2.96	11.058	-0.185	1.70
Cs_2UBr_6	11.070 [56]	1.88	0.89	1.96	0.79	1.7	2.96	11.009	0.061	0.55
Cs_2WBr_6	10.733 [57]	1.88	0.66	1.96	0.79	1.7	2.96	10.784	-0.051	0.47
K_2OsBr_6	10.300 [34]	1.64	0.63	1.96	0.82	2.2	2.96	10.245	0.055	0.53
K_2PtBr_6	10.293 [37]	1.64	0.625	1.96	0.82	2.2	2.96	10.240	0.053	0.51
K_2ReBr_6	10.385 [37]	1.64	0.63	1.96	0.82	1.9	2.96	10.268	0.117	1.13
K_2SeBr_6	10.4224 [58]	1.64	0.50	1.96	0.82	2.55	2.96	10.091	0.331	3.18
K_2SnBr_6	10.480 [55]	1.64	0.69	1.96	0.82	1.96	2.96	10.322	0.158	1.50
K_2TeBr_6	10.780 [59]	1.64	0.97	1.96	0.82	2.1	2.96	10.586	0.194	1.80
Rb_2PdBr_6	10.020 [60]	1.72	0.615	1.96	0.82	2.2	2.96	10.388	-0.368	3.67
Rb_2SnBr_6	10.580 [55]	1.72	0.69	1.96	0.82	1.96	2.96	10.479	0.101	0.95
Rb_2TeBr_6	10.713 [61]	1.72	0.97	1.96	0.82	2.1	2.96	10.743	-0.030	0.28
Rb_2UBr_6	10.940 [56]	1.72	0.89	1.96	0.82	1.7	2.96	10.695	0.245	2.24
Rb_2WBr_6	10.489 [62]	1.72	0.66	1.96	0.82	1.7	2.96	10.470	0.019	0.18
Rb_2PdI_6	11.185 [63]	1.72	0.615	2.2	0.82	2.2	2.66	11.071	0.114	1.02
Rb_2PtI_6	11.217 [64]	1.72	0.625	2.2	0.82	2.2	2.66	11.081	0.136	1.21

Rb_2SnI_6	11.620 [65]	1.72	0.69	2.2	0.82	1.96	2.66	11.163	0.457	3.93
Cs_2HfI_6	11.609 [66]	1.88	0.71	2.2	0.79	1.3	2.66	11.547	0.062	0.53
Cs_2PdI_6	11.332 [67]	1.88	0.615	2.2	0.79	2.2	2.66	11.386	-0.054	0.47
Cs_2PoI_6	11.790 [68]	1.88	0.94	2.2	0.79	2.0	2.66	11.720	0.070	0.60
Cs_2PtI_6	11.158 [64]	1.88	0.625	2.2	0.79	2.2	2.66	11.395	-0.237	2.13
Cs_2SnI_6	11.650 [65]	1.88	0.69	2.2	0.79	1.96	2.66	11.477	0.173	1.48
Cs_2TeI_6	11.700 [69]	1.88	0.97	2.2	0.79	2.1	2.66	11.741	-0.041	0.35

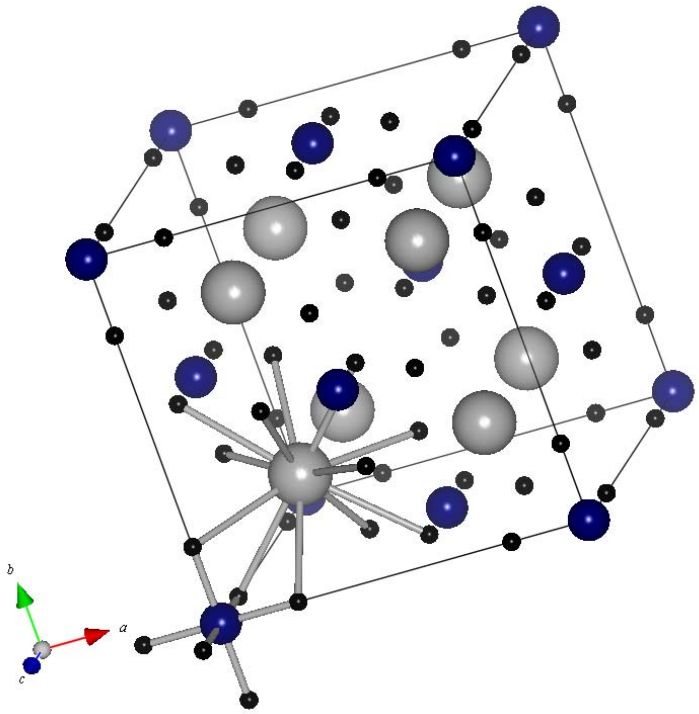

Fig. 1. One unit cell of the A_2XY_6 compounds (Fm-3m space group). The A cations are shown by large grey spheres, the X cations – by middle-size dark-blue spheres, and the halogen ions – by small black spheres. For the simplicity of the figure, only 6 X-Y and 12 A-Y chemical bonds are shown. Drawn with VICS-II developed by Izumi and Dilanian.

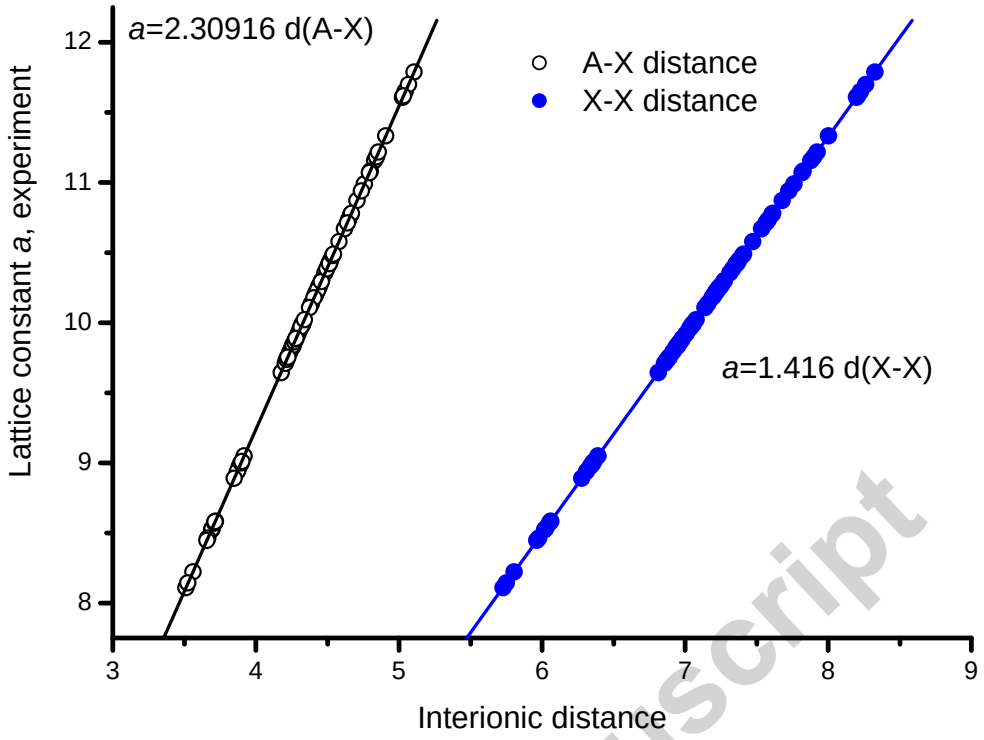

Fig. 2. Linear relation between the A-X and X-X interionic distances and crystal lattice constant for the A_2XY_6 cubic compounds (the axes units are Å).

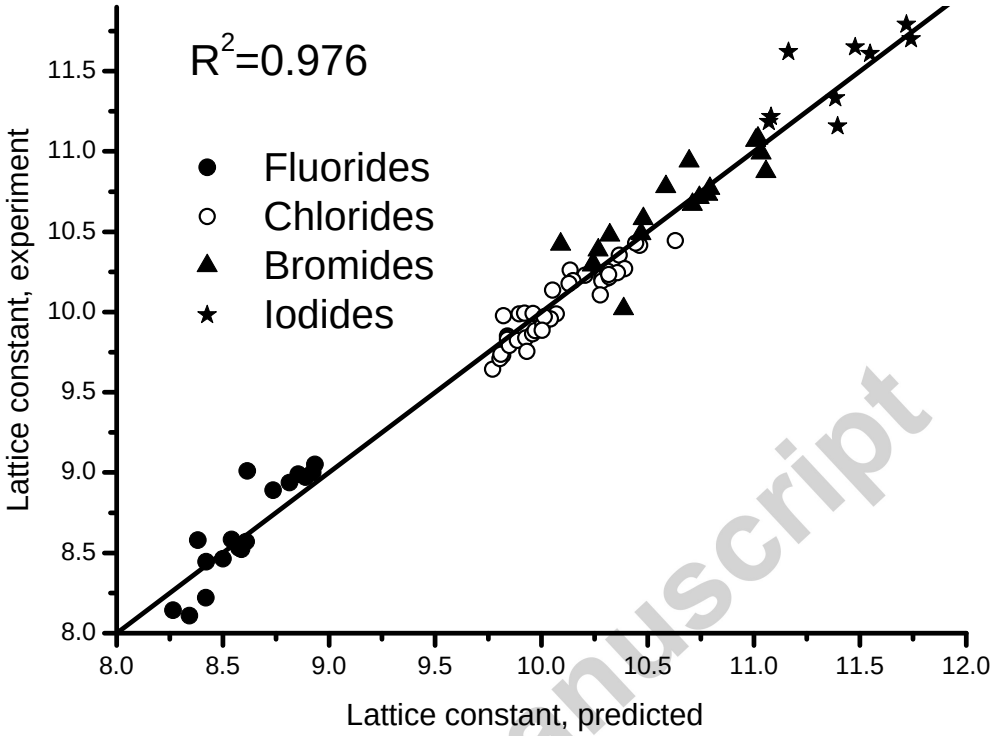

Fig. 3. Comparison between the predicted and experimental lattice constants for the A_2XY_6 compounds (the axes units are Å). The straight line has a slope of 1; it would correspond to the perfect match between the model's prediction and experimental data and is plotted as a guide to the eye. The correlation coefficient R^2 shows the quality of the linear fit.

Structural properties of the A_2XY_6 cubic crystals were thoroughly analyzed.

Relation between the lattice constant, ionic radii, electronegativity was derived.

Excellent agreement between predicted and experimental lattice constants was reached.

The derived relation can predict lattice constants of new materials from this group.