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Lattice Constants of Cubic K_2PtCl_6 type Structured Solids

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Abstract: *In this work, a semi-empirical model to describe and predict the lattice constants for a series of cubic crystals, all of which have the A_2BC_6 composition (A = K, Cs, Rb, Tl; B = tetravalent cation, C= 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 semi-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. The developed approach can be efficiently used for a simple, fast, and reliable prediction of lattice constants and inter ionic distances in isostructural materials having a similar composition.*
Key word*: Lattice Constants; Ionic radii; electronegativity*

I. Introduction

Lattice constant of solids may be measured by an experimental process such as X-ray, electron or neutron diffraction techniques. The experimental techniques used for determination of the crystal lattice parameters require special sophisticated equipment. Recent developments in modeling, through the use of density functional theory (DFT) and the increased availability of computational power, have made predictions of solid-state properties ab initio from theoretical principles relatively straightforward [1,2]. Hence it is now common to see calculations for the solid-state properties of binary and ternary compounds. Experimental data to verify these predictions are sparse, especially for non-equilibrium systems, and it can be difficult to interpret the accuracy of published data [3,4]. The difference between the experimental lattice parameters and theoretical (using computation) for the same crystal typically does not exceed a few percent on average. However, these techniques are usually complicated, difficult and time-consuming.

A number of theoretical calculations based on semi-empirical relations have become an essential part of material research. In many cases empirical relations do not give highly accurate results for each specific material, but they still can be very useful. In particular, the simplicity of empirical relations allows a broader class of researchers to calculate useful properties, and often trends become more evident. As a result, analytical and semiempirical methods need to be elaborated in concert with computational approaches and estimations. Empirical concepts such as valence, empirical radii, ionicity and plasmon energy are then useful [5-7]. These concepts are directly associated with the character of the chemical bond and thus provide means for explaining and classifying many basic properties of molecules and solids.

Cubic crystals with their single crystal lattice parameter (a) are of particular interest for empirical analysis of relationship between the lattice parameter and properties of particular chemical elements. In this paper, we present a semi-empirical relation for A_2BC_6 composition (A = K, Cs, Rb, Tl; B = tetravalent cation, C= F, Cl, Br, I) cubic crystals.

II. Theory, Results and Discussion

The lattice constant values for solid materials is of recognized importance, owing to the development of new solids designed for different applications, such as ferroelectric thin films, microwave and semiconductor technologies etc. [8]. Some empirical models were established that can predict lattice constant of solid materials from selected atomic properties of their constituent elements [4, 5, 9].

Recently, Brik et al. [10] predicted the lattice constant of A_2BC_6 composition (A = K, Cs, Rb, Tl; B = tetravalent cation, C= F, Cl, Br, I) cubic K_2PtCl_6 type structured solids by using the known ionic radii (R) and electronegativity (χ) of the materials. According to them the lattice constant may be determine by the following relation,

$$a\ (\text{in Å}) = 1.96325\ (R_A + R_B) + 0.98102\ (R_B + R_C) + 0.07593\ (\chi_C - \chi_B) + 0.57901 \qquad (1)$$

The author in previous research [4, 5] found that lattice constant was linear function of average ionic radii (R_{avg}) of the materials. Thus equation (1) must be substantially reduced in average ionic radii (R_{avg}) and average electronegativity (χ_{avg}) of the materials to get better agreement with experimental values and simplicity of the model. Similarly, based on the above expression and discussion, we are of the view that lattice constant

can be evaluated using their product of average ionic radii (R_{avg}) and average electronegativity (χ_{avg}) of these materials by following relation,

$$a \text{ (in Å)} = S + V\,(R_{avg})^3(\chi_{avg})^{0.1} \quad (2)$$

The constants S and V are given in table 1 along with the correlation coefficient (R) obtained from the regression analysis.

Table no 1: Linear regression results from the data for A_2BC_6 composition.

Properties	S	V	R
Lattice constant (a)	6.83345±0.11574	1.0617±0.03714	0.90778

A unique description of any crystal structure can be provided by the set of the crystal lattice parameters and atomic (ionic) positions. The knowledge of lattice constant is necessary in order to come to a better theoretical understanding of the material properties. It has been verified [10] that lattice constant assume a linear trend with ionic radii and electronegativity. We have plotted the curve between a_{exp} Vs $(R_{avg})^3(\chi_{avg})^{0.1}$ (R_{avg} = average of ionic radii, χ_{avg} = average of electronegativity) for the A_2BC_6 composition (A = K, Cs, Rb, Tl; B = tetravalent cation, C= F, Cl, Br, I), K_2PtCl_6 type-cubic crystals. We observe that in the plot of a_{exp} Vs $(R_{avg})^3(\chi_{avg})^{0.1}$, the A_2BC_6 compounds exhibit a linear line for all groups and data are presented in the following figure 1.

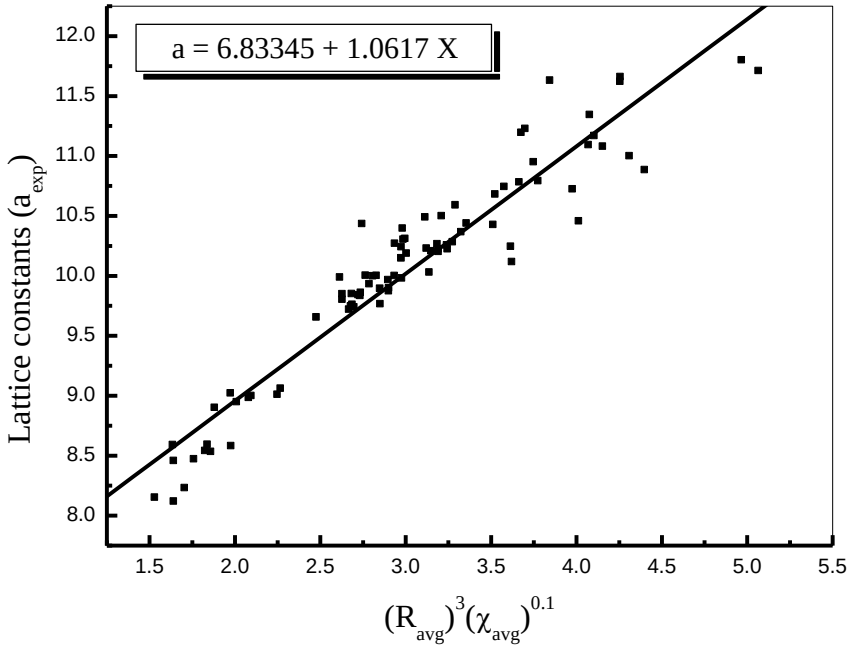

Figure 1. Lattice constants for A_2BC_6 composition (A = K, Cs, Rb, Tl; B = tetravalent cation, C= F, Cl, Br, I) as a function of $(R_{avg})^3(\chi_{avg})^{0.1}$. This line show linear relationship as determined by regression analysis. In this figure experimental lattice constant values are taken from Reference [10].

Table no 2: Values of experimental and predicted lattice constants, ionic radii and electronegativity for A_2BC_6 compounds,

Compounds	R_A [10]	R_B [10]	R_C [10]	R_{avg}	χ_A [10]	χ_B [10]	χ_C [10]	χ_{avg}	a (Å) Exp [10]	a (Å) this work	% error
Cs_2GeF_6	1.88	0.53	1.33	1.247	0.79	2.01	3.98	2.260	8.99	9.07	0.8
Cs_2MnF_6	1.88	0.53	1.33	1.247	0.79	1.55	3.98	2.107	8.97	9.05	0.9
Cs_2NiF_6	1.88	0.48	1.33	1.230	0.79	1.91	3.98	2.227	8.94	8.97	0.4
Cs_2PdF_6	1.88	0.615	1.33	1.275	0.79	2.2	3.98	2.323	9.00	9.23	2.5
Cs_2PtF_6	1.88	0.625	1.33	1.278	0.79	2.2	3.98	2.323	9.05	9.25	2.2
Cs_2SiF_6	1.88	0.4	1.33	1.203	0.79	1.9	3.98	2.223	8.89	8.84	0.6
Rb_2CrF_6	1.72	0.55	1.33	1.200	0.82	1.66	3.98	2.153	8.52	8.81	3.4

Rb_2GeF_6	1.72	0.53	1.33	1.193	0.82	2.01	3.98	2.270	8.58	8.79	2.4
K_2HfF_6	1.64	0.71	1.33	1.227	0.82	1.3	3.98	2.033	9.01	8.94	0.8
K_2MnF_6	1.64	0.53	1.33	1.167	0.82	1.55	3.98	2.117	8.22	8.65	5.2
K_2NiF_6	1.64	0.48	1.33	1.150	0.82	1.91	3.98	2.237	8.11	8.58	5.9
Rb_2MnF_6	1.72	0.53	1.33	1.193	0.82	1.55	3.98	2.117	8.53	8.78	2.9

Table 2 Continued ……

Rb_2NiF_6	1.72	0.48	1.33	1.177	0.82	1.91	3.98	2.237	8.46	8.71	2.9
Rb_2PdF_6	1.72	0.615	1.33	1.222	0.82	2.2	3.98	2.333	8.57	8.94	4.3
Rb_2SiF_6	1.72	0.4	1.33	1.150	0.82	1.9	3.98	2.233	8.45	8.58	1.6
Tl_2SiF_6	1.7	0.4	1.33	1.143	1.8	1.9	3.98	2.560	8.58	8.58	0.0
Cs_2GeCl_6	1.88	0.53	1.81	1.407	0.79	2.01	3.16	1.987	10.23	10.00	2.3
Cs_2IrCl_6	1.88	0.625	1.81	1.438	0.79	2.2	3.16	2.050	10.21	10.23	0.2
Cs_2MoCl_6	1.88	0.65	1.81	1.447	0.79	2.16	3.16	2.037	10.21	10.28	0.7
Cs_2PbCl_6	1.88	0.775	1.81	1.488	0.79	1.8	3.16	1.917	10.42	10.57	1.5
Cs_2PtCl_6	1.88	0.625	1.81	1.438	0.79	2.2	3.16	2.050	10.19	10.23	0.4
Cs_2ReCl_6	1.88	0.63	1.81	1.440	0.79	1.9	3.16	1.950	10.26	10.22	0.3
Cs_2SeCl_6	1.88	0.5	1.81	1.397	0.79	2.55	3.16	2.167	10.26	9.96	2.9
Cs_2SnCl_6	1.88	0.69	1.81	1.460	0.79	1.96	3.16	1.970	10.36	10.37	0.1
Cs_2TaCl_6	1.88	0.68	1.81	1.457	0.79	1.5	3.16	1.817	10.27	10.32	0.4
Cs_2TiCl_6	1.88	0.61	1.81	1.433	0.79	1.54	3.16	1.830	10.22	10.15	0.6

Table 2 Continued……

Cs_2WCl_6	1.88	0.66	1.81	1.450	0.79	1.7	3.16	1.883	10.25	10.28	0.4
Cs_2ZrCl_6	1.88	0.72	1.81	1.470	0.79	1.33	3.16	1.760	10.43	10.40	0.2
K_2MnCl_6	1.64	0.53	1.81	1.327	0.82	1.55	3.16	1.843	9.64	9.47	1.8
K_2MoCl_6	1.64	0.65	1.81	1.367	0.82	2.16	3.16	2.047	9.85	9.74	1.1
K_2OsCl_6	1.64	0.63	1.81	1.360	0.82	2.2	3.16	2.060	9.73	9.70	0.3
K_2PdCl_6	1.64	0.615	1.81	1.355	0.82	2.2	3.16	2.060	9.71	9.67	0.4
K_2PtCl_6	1.64	0.625	1.81	1.358	0.82	2.2	3.16	2.060	9.75	9.69	0.6
K_2ReCl_6	1.64	0.63	1.81	1.360	0.82	1.9	3.16	1.960	9.84	9.69	1.5
K_2RuCl_6	1.64	0.62	1.81	1.357	0.82	2.2	3.16	2.060	9.74	9.68	0.6
K_2SnCl_6	1.64	0.69	1.81	1.380	0.82	1.96	3.16	1.980	9.99	9.82	1.7
K_2TaCl_6	1.64	0.68	1.81	1.377	0.82	1.5	3.16	1.827	9.99	9.78	2.2
K_2TcCl_6	1.64	0.645	1.81	1.365	0.82	2.1	3.16	2.027	9.83	9.73	1.0
K_2TiCl_6	1.64	0.61	1.81	1.353	0.82	1.54	3.16	1.840	9.79	9.63	1.6
K_2WCl_6	1.64	0.66	1.81	1.370	0.82	1.7	3.16	1.893	9.82	9.74	0.8
Rb_2MnCl_6	1.72	0.53	1.81	1.353	0.82	1.55	3.16	1.843	9.84	9.63	2.1

Table 2 Continued……

Tl_2MoCl_6	1.7	0.65	1.81	1.387	1.8	2.16	3.16	2.373	9.86	9.92	0.6
Rb_2NbCl_6	1.72	0.68	1.81	1.403	0.82	1.6	3.16	1.860	9.99	9.96	0.3
Rb_2PbCl_6	1.72	0.775	1.81	1.435	0.82	1.8	3.16	1.927	10.20	10.18	0.1
Rb_2PdCl_6	1.72	0.615	1.81	1.382	0.82	2.2	3.16	2.060	9.99	9.84	1.5
Rb_2PtCl_6	1.72	0.625	1.81	1.385	0.82	2.2	3.16	2.060	9.88	9.87	0.2
Tl_2PtCl_6	1.7	0.625	1.81	1.378	1.8	2.2	3.16	2.387	9.76	9.87	1.1
Rb_2SeCl_6	1.72	0.5	1.81	1.343	0.82	2.55	3.16	2.177	9.98	9.62	3.6
Rb_2SnCl_6	1.72	0.69	1.81	1.407	0.82	1.96	3.16	1.980	10.14	10.00	1.4
Rb_2TiCl_6	1.72	0.61	1.81	1.380	0.82	1.54	3.16	1.840	9.92	9.80	1.2
Rb_2WCl_6	1.72	0.66	1.81	1.397	0.82	1.7	3.16	1.893	9.96	9.92	0.4
Rb_2ZrCl_6	1.72	0.72	1.81	1.417	0.82	1.33	3.16	1.770	10.18	10.03	1.5
Tl_2SnCl_6	1.7	0.69	1.81	1.400	1.8	1.96	3.16	2.307	9.97	10.00	0.3

Tl_2WCl_6	1.7	0.66	1.81	1.390	1.8	1.7	3.16	2.220	9.89	9.92	0.3

Table 2 Continued……

Cs_2NpBr_6	1.88	0.87	1.96	1.570	0.79	1.3	2.96	1.683	11.08	11.16	0.7
Cs_2PoBr_6	1.88	0.94	1.96	1.593	0.79	2	2.96	1.917	10.99	11.42	3.9
Cs_2PtBr_6	1.88	0.625	1.96	1.488	0.79	2.2	2.96	1.983	10.67	10.58	0.8
Cs_2SnBr_6	1.88	0.69	1.96	1.510	0.79	1.96	2.96	1.903	10.77	10.73	0.4
Cs_2TeBr_6	1.88	0.97	1.96	1.603	0.79	2.1	2.96	1.950	10.87	11.51	5.9
Cs_2UBr_6	1.88	0.89	1.96	1.577	0.79	1.7	2.96	1.817	11.07	11.25	1.6
Cs_2WBr_6	1.88	0.66	1.96	1.500	0.79	1.7	2.96	1.817	10.73	10.64	0.9
K_2OsBr_6	1.64	0.63	1.96	1.410	0.82	2.2	2.96	1.993	10.30	10.02	2.7
K_2PtBr_6	1.64	0.625	1.96	1.408	0.82	2.2	2.96	1.993	10.29	10.01	2.7
K_2ReBr_6	1.64	0.63	1.96	1.410	0.82	1.9	2.96	1.893	10.39	10.01	3.7
K_2SnBr_6	1.64	0.69	1.96	1.430	0.82	1.96	2.96	1.913	10.48	10.15	3.2
K_2TeBr_6	1.64	0.97	1.96	1.523	0.82	2.1	2.96	1.960	10.78	10.85	0.6
Rb_2PdBr_6	1.72	0.615	1.96	1.432	0.82	2.2	2.96	1.993	10.02	10.17	1.5
Rb_2SnBr_6	1.72	0.69	1.96	1.457	0.82	1.96	2.96	1.913	10.58	10.34	2.3

Table 2 Continued……

Rb_2TeBr_6	1.72	0.97	1.96	1.550	0.82	2.1	2.96	1.960	10.71	11.06	3.3
Rb_2UBr_6	1.72	0.89	1.96	1.523	0.82	1.7	2.96	1.827	10.94	10.82	1.1
Rb_2WBr_6	1.72	0.66	1.96	1.447	0.82	1.7	2.96	1.827	10.49	10.25	2.3
Rb_2PdI_6	1.72	0.615	2.2	1.512	0.82	2.2	2.66	1.893	11.19	10.74	4.0
Rb_2PtI_6	1.72	0.625	2.2	1.515	0.82	2.2	2.66	1.893	11.22	10.77	4.0
Cs_2HfI_6	1.88	0.71	2.2	1.597	0.79	1.3	2.66	1.583	11.61	11.36	2.2
Cs_2PdI_6	1.88	0.615	2.2	1.565	0.79	2.2	2.66	1.883	11.33	11.17	1.4
Cs_2PoI_6	1.88	0.94	2.2	1.673	0.79	2	2.66	1.817	11.79	12.11	2.7
Cs_2PtI_6	1.88	0.625	2.2	1.568	0.79	2.2	2.66	1.883	11.16	11.20	0.3
Cs_2SnI_6	1.88	0.69	2.2	1.590	0.79	1.96	2.66	1.803	11.65	11.36	2.5

III. Summary and Conclusions

We developed a semi-empirical model for lattice constants of cubic K_2PtCl_6 type structured solids. It is quite obvious that the lattice constant reflecting the structural property can be expressed in terms of the product of average electronegativity and average ionic radii of these materials. The calculated values are presented in Tables 2 and hardly deviates 0–6% from experimental data. The values evaluated show a systematic trend and are consistent with the available data reported so far, which proves the validity of the approach. It is also noteworthy that proposed empirical relation is simpler, widely applicable and values obtained are in better agreement with experiment data as compared to the empirical relations proposed by previous researchers. The method presented in this work will be helpful to material scientists for finding new materials with desired lattice constant among a series of structurally similar materials.

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