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First-principles Study of the Correlation between Host Components and Properties of $IAIIAF_3$ Cubic Perovskite Compounds

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Abstract. For the first time the structural, elastic and band gap properties of 10 perovskite crystals $IAIIAF_3$(IA=K, Rb; IIA=Be, Mg, Ca, Sr, Ba) were calculated systematically using the CRYSTAL09 program. Several trends in the variation of these properties in relation to the Ionic radius R of the alkaline-earth metals ions were found. In particular, the lattice parameter of these compounds increases with R, whereas the elastic constants and band gap decrease. The Research of above properties will be very helpful in order to further improve their performances on the high-technology applications.

Keywords: Perovskite structural and elastic properties First-principle calculations

1. Introduction

Fluoroperovskites is a common name for a large group of crystals with the general chemical formula $IAIIAF_3$ where the IA are the univalent cations of the alkali-metals and IIA are the divalent cations of the alkaline-earth metals. All chosen compounds crystallize in the *Fm-3m* structure (Space Group No. 225). Those types of compounds have attracted increasing attention recently because of its excellent physical and chemical properties. Also, its application covers the ferroelectric [1] piezoelectric [2], catalytic action [3], colossal magnetoresistance [4] and iron [5, 6], superconductor [7-9], battery electrode [10] and other aspects. Moreover, perovskite crystal structure is one of the most common type of structure of inorganic solid state chemistry, and most of the perovskite compounds are oxide and fluoride, so it's easy to synthesis in the laboratory. Based on these special properties, perovskite halide has great potential in new materials application fields.

In fact, those types of compounds have been partially researched before, but never at such scale. In the early 80s, Brauch and Durr proved that the $KMgF_3$: Cr^{3+} and $CsCaF_3$: V^{2+} crystal could be used as a near infrared spectral region of tunable laser active element in Ref. [12].The pressure effects on the elastic, electronic and optical properties of KCaF3 were studied in Ref. [13] using the WIEN2K code. The $KCaF_3$ and $RbCaF_3$ perovskites were considered in Refs. [14, 15]. The structural, electronic and optical properties of $KCaF_3$ and $KCaCl_3$ were calculated in Ref. [16]. Finally, various approaches to study $CsCaF_3$ at ambient pressure were employed in Refs. [17-20]. It also can be noticed that the spectroscopic properties of various impurities in these perovskites were studied, for example, Ni^{2+} [21] and Gd^{3+} [22] in $RbCaF_3$, V^{2+} [23] and Cr^{3+} [24] in $CsCaF_3$, Pr^{3+} and Ce^{3+} in $KCaF_3$ [25].

With the development of technology and economy, it has been gradually become an urgent work to seek new cubic perovskite materials. It's unrealistic to synthesize all of them because of enormous workloads to synthesize all of them, which restricted the perovskite compounds application prospect in the field of new materials. However, with the developing of CPU performance and the decline of cost, it's fortunate to know that it is gradually possible to use theoretical software, such as CRYSTAL09 based on first-principles calculation, to compute and design new materials. This method has been gradually become a popular way to study the new compounds. Thus, in the present work, the CRYSTAL09 software was used to calculate and determine the reality structure of cubic perovskite crystals from two possible structures. Also, the properties of elastic and electronic were considered. This work could provide a reference to the experiment to some extent.

The structure of the paper is as follows: the method and details of calculations are described in Section 2. All calculated results along with corresponding discussions are collected in Section 3 (which is divided into several subsections for easier reading). Section 4 contains the main conclusions of the presented calculations.

2. Details of calculations

For the geometry optimization calculation: The convergence criteria on the root-mean-square (RMS) of the gradient and the nuclear displacement (TOLDEG and TOLDEX) were set to 0.00006 Hartree/Bohr and 0.00012 Bohr, respectively. The energy calculation precision setting was chosen as follows: the hybrid exchange-correlation functional WC1PBE consisting of a PBE correlation part and a Wu-Cohen exchange part with a fractional mixing (16%) of the nonlocal Hartree-Fock (HF) exchange was adopted in this study. An "extra extra large" pruned DFT integration grid (XXLGRID) was adopted. The Monkhorst–Packschem for 14×14×14 *k*-point mesh in the Brillouin zone (BZ) was applied; the truncation criteria for bielectronic integrals (Coulomb and HF exchange series) were set to 9, 9, 9, 9 and 18; Bipolar expansion approximation control was set as follows: 27 for Coulomb and 21 for exchange. The maximum cycle number was set to 900. The tolerance of the energy convergence on the self-consistent field (SCF) iterations (TOLDEE) was set to 10^{-10} Hartree. For the elastic constant calculation.

The Gaussian-type basis sets were employed as follows: K_pob_TZVP_2012 was used for K. Rb_SC_schoenes_2008 was used for Rb. Be_5-11G_lichanot_1992 [26] was used for Be.Mg_8-511d1G_valenzano_2006 [27] was used for Mg. Ca_86-511d21G-valenzano_2006 [28] was used for Ca. Sr_HAYWSC-311(1d) G_piskunov_2004 [29] was used for Sr. Ba_HAYWSC-311(1d) G_piskunov_2004 [30] was used for Ba. F_7-311G_nada_1993 was used for F [31].

After the crystal structures were optimized with the above-given computational settings, the electronic, elastic properties were calculated, all these results are presented below.

3. Results of calculations

3.1. Structural properties

All 10 perovskites were considered in the present paper, the first and the second cations are 12- and 6- fold coordinated by the fluorine ions, respectively. A summary of the structural data for the 10 perovskites are listed in table 1. As seen from the table, the lattice constants increase monotonically with increasing atomic number and ionic radii of the second cation (Be - Mg - Ca - Sr - Ba). The values of the lattice constants for those perovskites, for which we did not find any experimental data, are the theoretical estimations, which can be tested by experiment in future.

The relationship between optimized lattice constant of perovskites and the ionic radius r was shown in Fig. 1. The data could be fitted as the linear functions $a = 3.10181 + 1.4058\ r$ and $a = 2.9369 + 1.5179\ r$, with the correlation coefficient 0.98 and 0.99, respectively. In these equations, the lattice constant a is expressed in Å.

Table 1: The optimized lattice constants a (Å) and volume V (Å^3) of 10 ideal cubic perovskites. Experimental data (if available) are given in the parenthesis.

Formula	Lattice constant a (Å)	Volume V (Å^3)	Band gap E g (eV)
KBeF3	3.6714	49.4871	10.6871
KMgF3	3.9847	63.2675	9.4961
KCaF3	4.4175	86.0439	8.4377
KSrF3	4.7010	103.8911	8.0754
KBaF3	5.0447	128.3836	7.2486
RbBeF3	3.7924	54.5425	9.9596
RbMgF3	4.0658	67.2130	9.2079
RbCaF3	4.4593	88.4885	8.7727
RbSrF3	4.7316	105.9327	8.2838
RbBaF3	5.0671	130.1028	7.4947

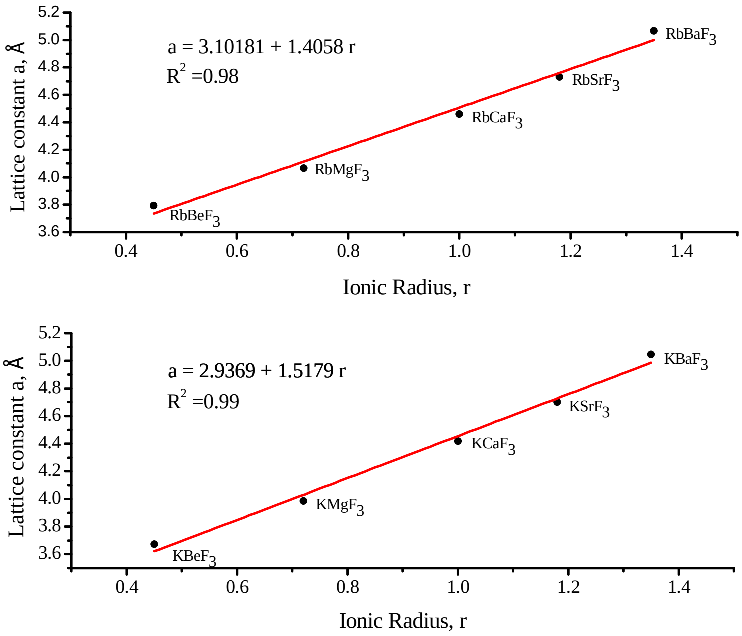

Figure 1. The optimized lattice constant (symbols) and their linear approximations as functions of ionic radius r for *IAIIA*F_3 (*IA*= K, Rb, *IIA*= Be, Mg, Ca, Sr, Ba) crystals. Equation of a linear fit is also given in the graph.

3.2. Elastic properties

Only three elastic constants C_{11}, C_{12}, C_{44} are required to describe completely the elastic properties of cubic crystals. These constants have been calculated with the computational settings described above. Using these constants, one can then estimate quite a number of important characteristic of the solid, such as the bulk modulus *B*, using the following equation

$$B = \frac{(C_{11} + 2C_{12})}{3}$$

Voigt's shear modulus G_V (an upper limit for *G* values) and Reuss's shear modulus G_R (a lower limit for *G* values) were calculated using the elastic constants C_{ij}

$$G_V = \frac{(C_{11} - C_{12} + 3C_{44})}{5}$$

$$\frac{5}{G_R} = \frac{4}{C_{11} - C_{12}} + \frac{3}{C_{44}} \text{[32].}$$

All the above referenced quantities are collected in Table 2, and the presenting trends in the groups of the perovskites studied in this work are visualized in Fig. 2. With increasing ionic radius (increasing lattice constants) elasticity modulus B decreases monotonously, which can be well fitted using the linear function.

Table 2: The calculated elastic constants C_{ij} (GPa), bulk moduli B (GPa), and shear moduli GV (GPa) for 10 cubic perovstike.

Formula	C_{11}	C_{22}	C_{44}	B	GV
KBeF3	145.257	94.828	111.017	111.638	76.696
KMgF3	143.068	40.902	49.835	74.957	50.334
KCaF3	124.083	18.878	19.226	53.946	32.577
KSrF3	107.709	13.818	11.301	45.115	25.559
KBaF3	87.565	11.029	6.261	36.541	19.064
RbBeF3	131.126	94.045	109.573	106.405	73.160
RbMgF3	129.365	44.910	55.704	73.062	50.313
RbCaF3	115.753	20.200	22.154	52.051	32.403
RbSrF3	101.763	14.156	13.031	43.358	25.340
RbBaF3	84.168	11.091	7.431	35.450	19.074

3.3. Electronic properties

Table 1 contains a summary of the band gaps data for the 10 studied perovskites. As seen from the comparison with the available experimental structural data, it is consistent with the experimental lattice constants. Also, all the band gaps data are exhibited in Fig. 3. It is observed that band gaps reveal a monotonic decrease with increasing atomic number.

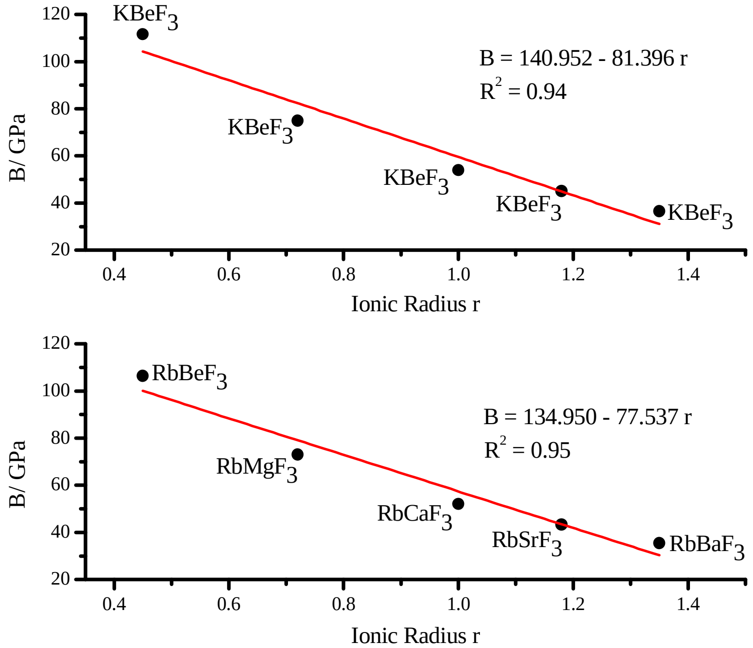

Figure 2. Calculated values of the elastic constants (symbols) and their linear fits (lines) of ionic radius r for $IAIIAF_3$ (IA= K, Rb, IIA= Be, Mg, Ca, Sr, Ba) crystals. Equations of the linear fits and the correlation coefficients are also given in the graph.

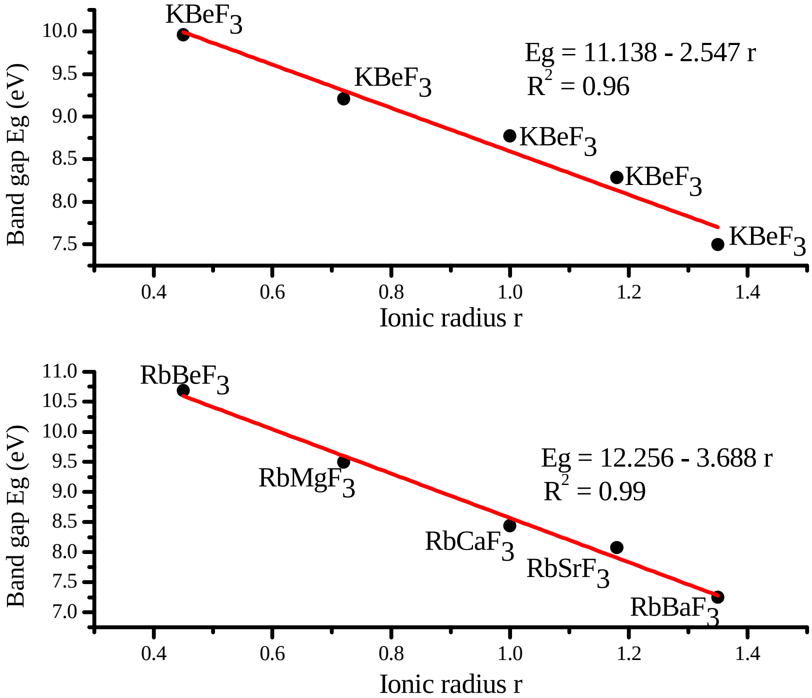

Figure 3. Calculated values of the band gap (symbols) and their linear fits (lines) of ionic radius r for *IAIIA*F_3 (*IA*= K, Rb, *IIA*= Be, Mg, Ca, Sr, Ba) crystals. Equations of the linear fits and the correlation coefficients are also given in the graph.

4. Conclusions

Detailed ab initio calculations of the structural, electronic and elastic properties of 10 fluoroperovskites *IAIIA*F_3 (*IA* = K, Rb; *IIA* = Be, Mg, Ca, Sr, Ba) have been performed in the present paper. Aggregate analysis of the above-mentioned properties exhibited correlation between the lattice constants, elastic constants, band gaps and atomic number of alkaline-earth metals: increasing of the atomic number of Be, Mg, Ca, Sr and Ba is followed by the linear growth of lattice constants, linear decrease of elastic constants and decline of band gaps. Hence, the alkaline-earth metals element which is in the center of crystal are the main factors for the structural, elastic and electronic properties of perovskite.

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