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Predicting lattice constant of complex cubic perovskites using computational intelligence

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ABSTRACT

Recently in the field of materials science, advanced computational intelligence (CI) based approaches are gaining substantial importance for modeling the quantitative structure to properties relationship. In this study, we have used support vector regression, random forest, generalized regression neural network, and multiple linear regression based CI approaches to predict lattice constants (LCs) of complex cubic perovskites. We have collected reasonable number of perovskites compounds from the recent literature of materials science. The CI models are developed using 100 training compounds and the generalized performance is estimated for the novel 97 compounds. Our analysis highlights the improved prediction performance of CI approaches than the well-known SPuDS software, which is extensively used in crytsallography. We further observed that, for some of the compounds, the larger prediction error provided by the CI models is correlated with the structure deviation of the compounds from its ideal cubic symmetry.

1. Introduction

In case of crystalline materials, lattice constants (LCs) not only play an important role in the identification of compounds but also help in assessing interesting material properties. In various industrial applications, it is important to have correct knowledge of lattice constants of unknown perovskites for synthesizing and analyzing structural properties. This assists in making a choice of suitable material in many industries related problems. For example, lattice mismatch between thin films and substrates is a familiar industrial concern. This restricts the fabrication of thin films at large scale [1]. In the epitaxial growth of thin film, in semiconductor industry, appropriate perovskites compounds are searched whose lattice constant (LC) is matched with the substrate. The reduced lattice mismatch improves the film quality [2]. Sr_2CrWO_6 perovskites on $SrTiO_3$ substrate, the lattice mismatch smaller than 0.13% is obtained. However, in order to avoid atomic disorder for a very narrow range of deposition temperature and atmosphere, metallic perovskites of Sr_2CrReO_6 and Sr_2FeMoO_6 are preferred for $SrTiO_3$ (0 0 1) substrates. The hetero-epitaxial growth with matching lattice structure of Ca_2FeMoO_6/Ca_2FeReO_6 compounds are feasible [3]. In these scenarios, the knowledge of precise prediction of LCs, especially of newly synthesized perovskites, is of prime importance.

Perovskites materials have many interesting physical, chemical, and catalytic properties. Due to the diverse physiochemical and transport properties, the complex cubic compounds are being used in numerous scientific and engineering applications to design dielectric resonators for wireless communication, piezoelectric, ferroelectric and optical devices [4], etc. For example, Sr_2FeMoO_6 and Sr_2FeReO_6 perovskites are used for half-metallic ferrimagnets, relaxer ferroelectric, low loss dielectric, and photocatalyst [5]. A useful application of perovskites compounds is the ferroelectric property that helps to retain a residual electric polarization for permanent dipole. This interesting property can be used for the development of random access memories to retain the stored information. The physiochemical applications of perovskites material are also investigated for various applications. These growing applications of perovskites material impel researchers for modeling the structural properties relationship of perovskites. The increasing demand of synthesizing new perovskites compounds emphasizes to predict the structure of unit cell. Chemical stoichiometry based SPuDS software is used to predict the structural information of newly synthesized perovskites [6]. This program uses the bond valence parameters and nominal cation oxidation states.

Advancement in high performance computing techniques allowed the researchers to develop Density-Functional Theory

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(DFT) based computational tools [7–10]. DFT tools are based on the first principles of quantum mechanics to solve the Schrodinger equation in which total energy of the system is minimized through density functional equation. DFT approach is used in predicting the physiochemical properties of compounds [11–14]. The software tools based on DFT estimate the electronic structure of atomic/molecular and elastics properties of compounds separately [15–18]. Using DFT tools, one can estimate atomic/molecular structure and lattice parameters of perovskites. However, while using DFT tools, a chemist/engineer need significant computational resource [19] and sufficient in-depth knowledge related to the electronic configuration, bonding energy, charge distribution, and states density of the material under study [20]. DFT models need nearly the same amount of computational resources/skill for each newly synthesized compound. On the other hand, in industrial/engineering applications, the computational intelligence (CI) based approaches have advantages over DFT approach. Once an optimal prediction model is developed for training data, then it can be effectively used in predicting the structural properties for novel compounds.

Initially, researchers proposed simple prediction models for the characterization and the identification of perovskites structure. multiple linear regression (MLR) models were developed to correlate LC with atomic parameters of simple cubic perovskites. However, simple linear models may compromise on accuracy for complex perovskites structure. Therefore, it is of practical interest to use computational intelligence (CI) based approaches where less human expertise or computational resources are available. These approaches are used extensively to predict various physiochemical properties of crystalline compounds [21–28] and amorphous metallic glass alloys [29,30]. In this study, we explored the learning capabilities of CI approaches to correlate LC with atomic parameters of complex cubic perovskites of $A_2BB'O_6$-type. We selected support vector regression (SVR), random forest (RF), generalized regression neural network (GRNN) and multiple linear regression (MLR) approaches. During the model developing stage, the optimal values of the model parameters are computed for training data. Then the model is used to predict the lattice parameter of novel compounds.

In one experiment, prediction models developed using only three features of ionic radii A, B, and B′. Further, the prediction capability explored for six features by adding three more variables corresponding to the values of electro-negativity and oxidation states of B and B′ ions. During training stage, the optimal parametric values for prediction models are extracted from the input training data. The performance of prediction models measured in terms of percentage absolute difference (*PAD*). Our analysis revealed the improved prediction of CI models. For three features, the overall *PAD* error of SVR, RF, GRNN and MLR models found 0.413, 0.395, 0.414, and 0.523, respectively. Further, for six features, overall *PAD* error of these models observed 0.261, 0.418, 0.700, and 0.517, respectively. These error values are significantly lower than the overall *PAD* value 1.582 given by SPuDS program.

The rest of paper is organized such that in Section 2, a brief description of input data collection is given and it is explained how prediction models are developed using various CI approaches. In Section 3, we discuss the simulated results and analyze the performance of prediction models. Finally, in Section 4, conclusions are provided.

2. Materials and methods

The inherent flexibility of chemical substitutions on both A and B-sites, perovskites compounds contribute to various types of crystal structures. Double cubic perovskites compounds, with a general chemical formula of $A_2BB'O_6$-type, are the result of doubling ABO_3 type unit cell. In case of ordered arrangement between B- and B′-cations, generally, a superstructure of perovskites is formed. The aristo type structure of double perovskites crystallizes in Fm3 m space group with cubic symmetry [31]. In this work, four diverse type of CI approaches are employed to develop expert system for $A_2BB'O_6$-type complex perovskites. The generic block diagram in Fig. 1 highlights how unknown parameters of each CI model are optimized. During training, CI based prediction models are developed by minimizing the *PAD* values. The performance of models is estimated for the novel data. The implementation detail of each model is explained in Section 2.2.

2.1. Data formation

The large variation in the valence and the radii between B- and B′-cations are mainly responsible for the structure of perovskites double cubic compounds to settle down in order/disorder way [32]. The physiochemical properties of the constituent ions are responsible in modeling the structure of perovskites. The unit cell of cubic compounds is represented with one parameter of lattice constant (LC). For this work, the values of the effective ionic radii of A, B and B′ are obtained (corresponding to specific values of oxidation states and coordination numbers) from Shannon's work [33]. In $A_2BB'O_6$-type cubic perovskites, A- and B-cations settle down to coordination numbers of twelve and six, respectively. The values of electro-negativity (x) of B- and B′-cations are taken using the Pauling's electro-negativity tables [34]. The dataset of 197 perovskites compounds are collected from the current literature. The detail list of six atomic parameters along with the experimental LC is given in Supplementary Tables 3 and 4.

From the input dataset, 100 compounds are randomly selected for models development and the remaining 97 compounds are used to evaluate the prediction models. It is to be noted that most of the compounds in the dataset belong to the structures of double cubic crystalline in *Fm3m* space group. However, there are a few orthorhombic and monoclinic types of compounds that are claimed to belonging the space group of *Pnma* and $P2_1/n$, respectively. In that case, we have used the pseudocubic LC.

2.2. Tolerance factor

In $A_2BB'O_6$-type perovskites, the tolerance factor (t) or bond valence parameter roughly estimates the distortion of BO_6 and $B'O_6$ octahedra from the cubic symmetry. We can anticipate the crystallographic structure of a double perovskite beforehand based on the distortion occurred between A-atom and O-atoms. It is observed in (A)$FeReO_6$ type perovskites that with the decrease of cation size, the crystallographic structure transform from cubic to tetragonal and monoclinic. The large lattice transformation occur in the monoclinic compounds [35]. In double perovskites, there are two possible ways to measure this distortion [3]. The tolerance factor t depends on the effective ionic radii of constituent ions as:

$$t = (r_A + r_O) \Big/ \left(\sqrt{2}(\langle r_{BB'} \rangle + r_O)\right), \tag{1}$$

$$t_{obs} = d_{A-O} \Big/ \left(\sqrt{2}(d_{B-O})\right), \tag{2}$$

where r_A and r_O represent the size of effective ionic radii (or Shannon ionic radii) of A- and O-atoms, respectively. The average ionic radius of B- and B′-atoms is denoted by $\langle r_{BB'} \rangle$. Here, d_{A-O} represents the averaged atomic distance between the A-atom and the nearest oxygen atom. Similarly, d_{B-O} is the averaged atomic distance between the B-atom and the nearest oxygen atom. Eq. (2) defines the observed tolerance factor (t_{obs}) that is near to the experimental approach. The value of t_{obs} gives accurate determination of the oxy-