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A.I. Chroneos¹, I.L. Goulatis², R.V. Vovk², A.A. Zavgorodniy²,
M.A. Obolenskii², A.G. Petrenko³, A.V. Samoilov²

ATOMISTIC MODELS FOR $R_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$
(R = Y AND LANTHANIDES) AND RELATED OXIDES

¹Institute of Microelectronics, NCSR Demokritos
Aghia Paraskevi 15310, Greece
E-mail: chroneos@imel.demokritos.gr

²Kharkov National University
4 Svoboda Sq., Kharkov, 61077, Ukraine
E-mail: Ruslan.V.Vovk@univer.kharkov.ua

³Donetsk National University
24 University St., Donetsk, 83055, Ukraine

Atomistic simulation techniques based on energy minimization have been employed to study the structural parameters of a series of orthorhombic $R_{1-x}Pr_xBa_2Cu_3O_{6.5}$ and related compounds. The new interatomic potential parameters have been derived by simultaneous fitting the properties of a series of oxides such as CuO, R_2O_3 , $RBa_2Cu_3O_{6.5}$ and $R_{1-x}Pr_xBa_2Cu_3O_{6.5}$ a total of 62 compounds. The predicted structural parameters have been compared with previous experimental and theoretical studies yielding excellent agreement. The aim of this work is to generate transferable potentials that can be applied as the basis for future theoretical studies of the defect chemistry of cuprate superconductors and other technologically important oxides.

Introduction

$RBa_2Cu_3O_7$ (R = Y and lanthanides) compounds are of technological importance as high-temperature superconductors since their critical temperature T_c is about 90 K. It should be stressed that Ce and Tb do not form the orthorhombic structure [1], Pm is radioactive, and $PrBa_2Cu_3O_7$ is non-metallic and non-superconducting («praseodymium anomaly») even though it exhibits the orthorhombic unit cell [2]. $PrBa_2Cu_3O_7$ is important as the investigation of the presence or absence of superconductive properties in compounds of identical crystal structure and the understanding of the conditions under which the phenomenon is not present can be important. This is evident by the amount of experimental work aiming at explaining the «praseodymium anomaly» [3]. The structure-property relationships are tech-

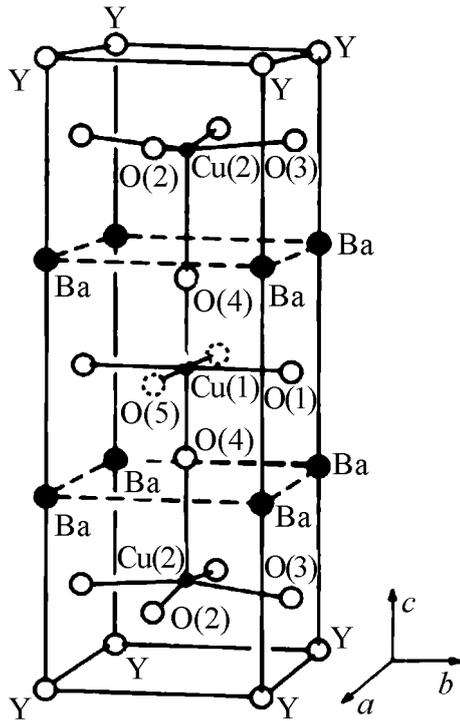


Fig. 1. The orthorhombic unit cell and atom labelling of $\text{YBa}_2\text{Cu}_3\text{O}_7$ [5]

in the a - b plane. The R^{3+} and Ba^{2+} ions provide an effective framework that bounds the copper oxide. The orthorhombic unit cell of $\text{YBa}_2\text{Cu}_3\text{O}_7$ is presented in Fig. 1. The $\text{R}\text{Ba}_2\text{Cu}_3\text{O}_{6.5}$ considered has a closely related crystal structure and only differs by the partial occupancy of the O(1) oxygen ions. In $\text{R}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{6.5}$ there is partial occupancy of the R^{3+} sites by the praseodymium atoms.

The aim of this work is to introduce a transferable two-body potential model that can describe the structure of a series of oxides including CuO , R_2O_3 , $\text{R}\text{Ba}_2\text{Cu}_3\text{O}_{6.5}$ and $\text{R}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{6.5}$. To illustrate the applicability of the atomic scale techniques the dependence of the lattice parameters and interatomic distances of a series of $\text{R}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{6.5}$ ($x = 0.25, 0.5$ and 0.75) on the ionic radius of R^{3+} and the Pr content has been determined. Even though pair potentials have limits they are able to model large numbers of atoms. Consequently the potential models developed in this study can be applied to simulate the defect chemistry of these materials.

Computational techniques

This study is based on the classical Born model description of the lattice [8]. Thus, the interaction between a pair of ions, $E(r_{ij})$, is given by

$$E(r_{ij}) = \frac{q_i q_j}{r_{ij}} + A_{ij} \exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6},$$

nologically significant because of the application of high-temperature cuprate superconductors [3]. For example, oxygen vacancies are modulating the hole doping of the Cu-O planes that in turn are critically important for the superconductivity of cuprates. There have previously been a number of atomistic simulation studies of cuprate superconductors including the structural and defect properties of $\text{R}_2\text{MCu}_2\text{O}_6$ ($\text{R} = \text{La}, \text{Nd}, \text{Y}$; $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) [4], the ionic and electronic defects in $\text{YBa}_2\text{Cu}_3\text{O}_7$ (YBCO) [5] and the defect chemistry in $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ [6].

$\text{R}\text{Ba}_2\text{Cu}_3\text{O}_7$ exhibits the orthorhombic structure (space group $Pmmm$, No. 47) [7] with a range of lattice parameters depending on the rare-earth ion. In this orthorhombic structure there exist two independent Cu sites consisting of square-planar CuO_3 chains and square-pyramidal CuO_2 planes in

where the first term is the Coulomb interaction between a pair of ions, the second term represents the short-range repulsive interaction and the third term is the van der Waals energy. In this equation r_{ij} is the separation between ions i and j and A_{ij} , ρ_{ij} and C_{ij} are adjustable parameters specific to the given pair of ions. It is important to appreciate that a single set of potentials has been derived to model all these structures in order to support further studies of more complex systems in future. The Buckingham interatomic potential parameters are reported in Table 1.

Table 1

Buckingham interatomic potential parameters

| Interaction | A , eV | ρ , Å ⁻¹ | C , eV·Å ⁻⁶ |
|-----------------------------------|----------|--------------------------|--------------------------|
| O ²⁻ -O ²⁻ | 9547.96 | 0.21916 | 32.0 |
| Cu ²⁺ -O ²⁻ | 3859.2 | 0.245 | 15.5 |
| Ba ²⁺ -O ²⁻ | 905.7 | 0.3976 | 0.0 |
| Y ³⁺ -O ²⁻ | 1766.4 | 0.3385 | 0.0 |
| La ³⁺ -O ²⁻ | 2078.5 | 0.3467 | 15.55 |
| Pr ³⁺ -O ²⁻ | 2004.6 | 0.3415 | 14.2 |
| Nd ³⁺ -O ²⁻ | 1975.2 | 0.3404 | 13.8 |
| Sm ³⁺ -O ²⁻ | 1941.9 | 0.34 | 12.55 |
| Eu ³⁺ -O ²⁻ | 1888.6 | 0.34 | 12.2 |
| Gd ³⁺ -O ²⁻ | 1855.9 | 0.339 | 11.9 |
| Tb ³⁺ -O ²⁻ | 1838.2 | 0.3385 | 14.5 |
| Dy ³⁺ -O ²⁻ | 1787.4 | 0.338 | 10.94 |
| Ho ³⁺ -O ²⁻ | 1738.7 | 0.338 | 11.1 |
| Er ³⁺ -O ²⁻ | 1694.5 | 0.338 | 11.3 |
| Yb ³⁺ -O ²⁻ | 1624.2 | 0.338 | 13.5 |
| Lu ³⁺ -O ²⁻ | 1533.6 | 0.339 | 10.3 |

In all cases a single unit cell is repeated periodically through the space. The Coulomb forces are summed using Ewald's method [9], whereas the short-range forces are summed explicitly up to a cut-off value of 20 Å. For a given set of parameters, the lattice parameters and positions of ions within the unit cells are identified through energy minimization. The parameters were selected by fitting to an extensive set of oxides structures. The code GULP [10] was used for all simulations. GULP requires manual set up of the crystal structure, whereas accuracy depends on the precise fitting of the potential parameters.

Results and discussion

To extend the transferability the potential model derived for RBa₂Cu₃O_{6.5} and R_{1-x}Pr_xBa₂Cu₃O_{6.5} has also been fitted to a number of rare-earth oxides (R₂O₃). In previous studies the potential model has reproduced the lattice parameters of Sc₂O₃, Y₂O₃ and La₂O₃ to within 0.1% of the experimental values [11–13]. Shan-

non [14] has tabulated the ionic radii of the chemical elements for a range of possible coordination environments and oxidation states. In all the figures Shannon's [14] ionic radii r for oxidation number +3 and 8-fold coordination have been adopted.

To demonstrate the efficacy of the computational methodology applied to study orthorhombic cuprates, the structural parameters of $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$, $\text{PrBa}_2\text{Cu}_3\text{O}_{6.5}$ and $\text{ErBa}_2\text{Cu}_3\text{O}_{6.5}$ have been compared to previous studies. $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ has been selected as YBCO is one of the most studied superconductors. The predictions for lattice parameters, the Y–O and Cu–O distances for $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ have been compared with experimental and computational investigations [15] (Table 2). It is evident that the derived parameters are in excellent agreement with the experimental values. Furthermore, the volume per unit cell of $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ is predicted to 0.05%. The equivalent structural parameters of $\text{ErBa}_2\text{Cu}_3\text{O}_{6.5}$ have been compared to experimental results [16] and the Er–O and Cu–O distances have been predicted to within 0.3% whereas the volume per unit cell to 0.7% (Table 3). The structure-property relations of $\text{PrBa}_2\text{Cu}_3\text{O}_7$ are important because of the «praseodymium anomaly» and have been the subject of a number of crystallographic studies. The experimentally determined [17] structure of $\text{PrBa}_2\text{Cu}_3\text{O}_{6.54}$ has been compared to the predicted values (Table 4). The derived volume per unit cell is underestimated by 1.13%, a fact that can be partially attributed to the difference in the oxygen concentration between the experimental and calculated unit cell. The Pr–O and Cu–O distances have been predicted to within 0.7%.

Table 2

The determined structure of $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ compared with previous experimental and calculated data [15]

| Parameters | Experiment | Previous calculated data | This study |
|-----------------|------------|--------------------------|------------|
| $a, \text{Å}$ | 3.842 | 3.797 | 3.812 |
| $b, \text{Å}$ | 3.878 | 3.872 | 3.907 |
| $c, \text{Å}$ | 11.747 | 11.710 | 11.747 |
| Cu(1)–O(1) | 1.939 | 1.936 | 1.942 |
| Y–O(2) | 2.406 | 2.387 | 2.404 |
| $V, \text{Å}^3$ | 175.02 | 172.16 | 174.95 |

Table 3

The experimentally determined [16] and calculated structure of $\text{ErBa}_2\text{Cu}_3\text{O}_{6.5}$

| Parameters | Experiment | This study |
|-----------------|------------|------------|
| $a, \text{Å}$ | 3.835 | 3.785 |
| $b, \text{Å}$ | 3.879 | 3.877 |
| $c, \text{Å}$ | 11.751 | 11.831 |
| Cu(1)–O(1) | 1.918 | 1.924 |
| Er–O(2) | 2.378 | 2.372 |
| $V, \text{Å}^3$ | 174.81 | 173.61 |

Table 4

 The experimentally determined [17] and calculated structure of $\text{PrBa}_2\text{Cu}_3\text{O}_{6.5}$

| Parameters | Experiment | This study |
|-----------------|------------|------------|
| $a, \text{Å}$ | 3.914 | 3.850 |
| $b, \text{Å}$ | 3.919 | 3.948 |
| $c, \text{Å}$ | 11.727 | 11.701 |
| Cu(1)–O(1) | 1.960 | 1.967 |
| Pr–O(2) | 2.437 | 2.456 |
| $V, \text{Å}^3$ | 179.88 | 177.85 |

In this study the dependence of the lattice parameters, R^{3+} –O(2) and Cu(1)–O(1) distances on the rare-earth radius and the Pr content has been investigated systematically for a series of $\text{R}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{6.5}$ compounds. The larger rare-earth atoms increase the a and b unit cell parameters (Fig. 1) and effectively lead the Ba atoms to reposition within the cuprate block. This is enhanced because of the partial occupancy of the O(1) atoms that in turn increases the available space within the cuprate block. As a consequence, the increase in the rare-earth radius results in an increase of the a and b unit cell parameters and a reduction of the height (lattice parameter c) of the unit cell. This is confirmed by the experimental results [15–17] for $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$, $\text{PrBa}_2\text{Cu}_3\text{O}_{6.54}$ and $\text{ErBa}_2\text{Cu}_3\text{O}_{6.5}$ (Tables 2–4).

The average rare-earth radius influences the structure of the mixed rare-earth compounds. For example, Yb and Pr have an average Shannon [14] 8-fold ionic radius of 1.055 Å, which is close to the equivalent radius of Gd (1.053 Å). The lattice parameters of $\text{GdBa}_2\text{Cu}_3\text{O}_{6.5}$ and $\text{Yb}_{0.5}\text{Pr}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{6.5}$ differ by only 0.1%. The dependence on the average rare-earth radius is also evident on the lattice energy (Fig. 2). For the previous example, the lattice energies of $\text{GdBa}_2\text{Cu}_3\text{O}_{6.5}$ and $\text{Yb}_{0.5}\text{Pr}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{6.5}$ differ by only 0.04%. This structural relation has been verified for different combinations of rare-earth ions and all Pr contents.

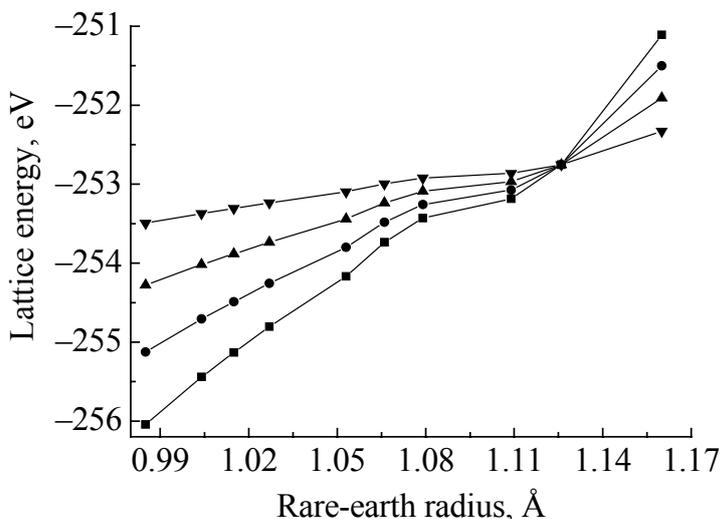


Fig. 2. Dependence of the lattice energy per unit cell on the Shannon [14] radii (8-fold coordination) and the Pr content of the $\text{R}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{6.5}$ compounds: ■ – 0.00, ● – 0.25, ▲ – 0.50, ▼ – 0.75

Conclusion

The results suggest that the average rare-earth ionic radius is critically important on the structure and energetics of $\text{R}\text{Ba}_2\text{Cu}_3\text{O}_{6.5}$ and $\text{R}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{6.5}$ compounds. The differences in the lattice parameters between the $\text{R}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{6.5}$ compounds are rectified with the increase of the Pr content. Energy minimization techniques can provide structural data comparable to the experimental determinations and of predictive nature that can be complementary to the experimental studies. These methods allow the systematic analysis of the complex behaviour and defect chemistry of these materials at the atomic level.

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A.I. Кронеос, І.Л. Гулатіс, Р.В. Вовк, А.А. Завгородній, М.О. Оболенський, О.Г. Петренко, О.В. Самойлов

АТОМІСТИЧНІ МОДЕЛІ ДЛЯ $\text{R}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ І СУПУТНІХ ОКСИДІВ

Атомістичні методи імітаційного моделювання, основані на принципі мінімізації енергії, використані для вивчення структурних параметрів ряду орторомбічних $\text{R}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{6.5}$ і пов'язаних з ними сполук. Нові міжатомні потенційні парамет-

ри взаємодії одержані для широкого діапазону оксидів, таких як CuO , R_2O_3 , $\text{R}\text{Ba}_2\text{Cu}_3\text{O}_{6.5}$ і $\text{R}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{6.5}$ (всього 62 сполуки). Одержані дані знаходяться в доброму узгодженні з попередніми результатами експериментальних і теоретичних досліджень. Мета даної роботи – прогнозування решітчастих потенціалів взаємодії, що можуть бути надалі використані як основа для теоретичного вивчення дефектної хімії надпровідних купратів та інших технологічно важливих оксидів.