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# Tuning of Metal−Metal Bonding by Counterion Size in Hypothetical $AeTiO_2$ Compounds

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No question that in predominantly ionic crystals cation or anion size may influence, greatly, unit cell dimensions and choice of structure type. We show here theoretical indications of significant cation-size tuning of a metal−metal bond in a partially ionic crystal.

We have been studying a *P*4/*mmm* $ABX_2$ structural type (Figure 1) suggested by M. J. Bucknum, who termed it "Kentuckia".[1] Its already realized examples are $CaCuO_2$[2] and $SrFeO_2$.[3] In the course of exploring variants of this structure, we came upon a hypothetical $SrTiO_2$ compound.

The undercoordinated Ti (and Sr) is obvious. What emerged from DFT calculations was a locally stable structure (confirmed by computation of phonon modes; details provided in the Supporting Information (SI)) with an optimized lattice parameter $c = 3.647$ Å. That is also the Ti−Ti distance, and it is long, beyond what one would normally associate with a bond. But in the electronic structure of $SrTiO_2$ (formally $Ti^{2+}$) a surprise awaited us—a pattern of bands characteristic of a one-dimensional metal along *c* and a Ti−Ti overlap population (OP, calculated with the extended Hückel (eH) method) of 0.29, despite that long Ti−Ti separation.

Thinking the Ti atoms along *c* "wanted" to be closer together, we decided to let them, by trying three smaller alkaline earth (Ae) cations (Be, Mg, and Ca). For good measure, we also tried a larger one (Ba). Given the formal $d^2$ configuration, one should consider the magnetism of these structures. Using a supercell, we computed antiferromagnetic (AFM) and ferromagnetic (FM) structures for all the phases: the structures emerged nonmagnetic for Ae = Be, Mg, Ca, and Sr. In the barium analogue, however, the FM $BaTiO_2$ (0.26 $\mu_B$) is 0.06 eV per formula unit more stable than the AFM variant.

The results of structure optimization in the series are shown in Table 1. Not all of these compounds may be dynamically stable; in phonon calculations, the Be and Mg compounds show imaginary frequencies. On the other hand, $AeTiO_2$ with large counterions, Ae = Ca, Sr, or Ba, are all stable. There is a dramatic effect of the alkaline earth cation, Ae, on the *c* dimension in these compounds and a direct dependence on the cation size. For the smallest cations, the *c* axis length is in the range of typical Ti−Ti bonds; for the largest cations, it is very long. Yet there is still some Ti−Ti bonding at these long distances, as indicated by the overlap population (OP).

Where does the Ti−Ti bonding come from in this structure? The band structure of $CaTiO_2$ (Ti−Ti 3.332 Å) is shown in Figure 2. Notice the high dispersion band crossing the Fermi level (Γ→Z); it is largely made up of $d_{z^2}$ orbitals. Another band made up of $d_{xz}+d_{yz}$ is partially occupied. The behavior of the levels along the Γ→Z direction is characteristic of a one-dimensional metallic chain: $d_{z^2}$ band going sharply up, $d_{xz}+d_{yz}$ going down.[4,5] This bonding pattern is present in all five Kentuckia phases studied.

Representative orbitals at the top and bottom of the $d_{z^2}$ and $d_{xz}+d_{yz}$ bands are shown in Scheme 1. Since the bottom portions of each band are filled, we effectively have both σ and π bonding along *z*, an approach to a Ti═Ti double bond.

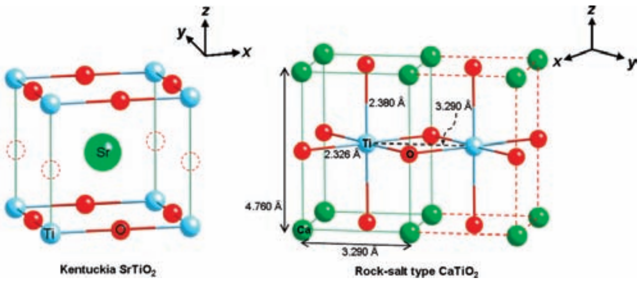


***Figure 1.*** Left: The *P*4/*mmm* Kentuckia structure ($ABX_2$), atoms specified for $SrTiO_2$. The relationship to the perovskite structure is emphasized in this view; a true perovskite would also include the atoms indicated by the dotted red empty circles. Right: An ordered rock-salt type $CaTiO_2$ structure.

***Table 1.*** Computed Lattice Constants (DFT) and the Ti−Ti Overlap Population Values (OP, eH) in Five Kentuckia $AeTiO_2$ Structures

| | *a* (Å) | *c* (Å) = Ti−Ti | Ti−Ti OP |
|---|---|---|---|
| $BeTiO_2$ | 3.911 | 2.856 | 0.36 |
| $MgTiO_2$ | 3.958 | 3.105 | 0.35 |
| $CaTiO_2$ | 3.993 | 3.332 | 0.34 |
| $SrTiO_2$ | 4.036 | 3.647 | 0.29 |
| $BaTiO_2$ | 4.075 | 4.129 | 0.23 |

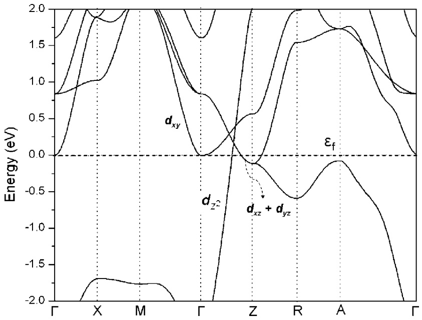
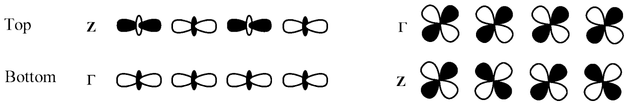


***Figure 2.*** Band structure of nonmagnetic $CaTiO_2$ (DFT), in a small energy window around the Fermi level.

***Scheme 1***



Ti(II) compounds, extended or molecular, are rare. Apart from TiO (defect rock-salt, much nonstoichiometry in this structure)[6,7] and the titanium halides $TiX_2$ (X = Cl, Br, I) which crystallize in the $CdI_2$ structure, there are very few other well-established Ti(II) extended structures.[8−10]

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***Table 2.*** Computed Reaction Energy (ΔE) for Five Hypothetical Reactions[a]

| reaction $\Delta E$ (eV) | $CaTiO_2$ | $SrTiO_2$ | $BaTiO_2$ |
|---|---|---|---|
| **(1)** $AeTiO_2 \rightarrow Ae + TiO_2$ | +1.57 | +1.46 | +1.25 |
| **(2)** $AeTiO_2 \rightarrow AeO + TiO$ | +0.20 | +0.69 | +0.98 |
| **(3)** $3AeTiO_2 \rightarrow Ti_2O + 2AeO + AeTiO_3$ | −0.08 | +0.29 | +0.81 |
| **(4)** $AeTiO_2 + {}^1/_2O_2 \rightarrow AeO + TiO_2$ | −4.69 | −4.30 | −4.07 |
| **(5)** $AeTiO_2 + {}^1/_2O_2 \rightarrow AeTiO_3$ | −4.96 | −6.39 | −5.31 |

[a] We used optimized structures for fcc Ca and Sr, bcc Ba, rutile $TiO_2$, rock-salt AeO and TiO.

Are the $AeTiO_2$ structures we propose realistic? We investigated computationally the potential decomposition or combustion reaction energy ($\Delta E$) of five pretty straightforward reactions shown in Table 2.

The first two simple alternative decomposition pathways, **(1)** and **(2)**, are endothermic, which is encouraging. **(3)** is exothermic only for $CaTiO_2$. We also looked at two reactions, **(4)** and **(5)**, involving $O_2$, the latter being the perovskite formation. These reactions were exothermic. Nothing surprising here, perovskites and $Ti^{4+}$ compounds are common structures. Before the synthesis of $SrFeO_2$ from its parent perovskite $SrFeO_3$ in 2007,[3] one might have viewed the great perovskite stability as an impediment to the existence of $AeTiO_2$ compounds. No longer; we think these compounds might be possible to make.

But one should think of other structural possibilities for $AeTiO_2$. Both TiO and CaO have a rock-salt structure, and Ca and Ti have similar ionic radii. So a rock-salt $CaTiO_2$ phase is a possibility.

We optimized the ordered rock-salt type $CaTiO_2$ structure shown in Figure 1 (right). This structural variant is 0.21 eV per $CaTiO_2$ more stable than Kentuckia (Figure 1, left) and is dynamically stable (no imaginary frequencies in phonon spectrum). The Ti−O distances are longer than a typical Ti−O bond: Ti−O bonds range from 1.92 to 1.98 Å in rutile, anatase and brookite $TiO_2$.[11,12] The nearest four Ti distances are long 3.290 Å, but the computed Ti−Ti OP (eH) is 0.19, indicating net bonding in the *ab* plane. For calibration, the Ti−Ti bond length in rutile $TiO_2$ is shorter, 2.959 Å, but the rutile Ti−Ti OP is only 0.02.

The magnetism of rock-salt $CaTiO_2$ is quite different from that of the Kentuckia structure. The AFM rock-salt structure (using a $\sqrt{2} \times \sqrt{2} \times 2$ supercell) is preferred to the FM alternative by 0.06 eV per $CaTiO_2$; the calculated Ti magnetic moment is 1.3 $\mu_B$.

The rock-salt structure is more stable than the Kentuckia geometry for Ae = Be (by −2.06 eV/$BeTiO_2$), Mg (−1.56 eV), and Ca (−0.21 eV) and less stable for Sr (+0.71 eV) and Ba (+1.94 eV). An analysis of the phonon modes for these structures is given in the SI.

What other structures might be reasonable? There is no dearth of alternatives. We began with what were perceived as related structures. A search of the Inorganic Crystal Structure Database (ICSD) revealed approximately a dozen $AMX_2$ (A = alkali metal or alkaline earth metal, X = O, S, Te, or N) structures with M = Ti, Zr, or Hf. None are formally $M^{2+}$ but rather $M^{3+,4+}$. $AeTiO_2$ was studied in three of the structural types found: $R3\bar{m}$ (e.g., $NaTiO_2$), $P4/nmm$ (e.g., $SrTiN_2$), $P\bar{3}m1$ (e.g., $LiTiS_2$), and $P6_3/mmc$ ($NaTiS_2$). The calculated energies per formula unit were significantly higher (>0.30 eV) for these structural alternatives, compared to the Kentuckia structure (see SI).

We moved next to evolutionary structure prediction, utilizing USPEX.[13−15] A USPEX search for $SrTiO_2$ and $BaTiO_2$ leads to the Kentuckia structures. For $CaTiO_2$, the lowest energy structure (−0.40 eV per $CaTiO_2$ relative to Kentuckia) was of rock-salt type, but one different from the previous rock-salt structure. Going along an −M−O−M−O−M− chain, this structure was not strictly alternating −Ti−O−Ca−O−Ti−O−Ca− but a less symmetrical variant. Clearly there are going to be many "polymorphs" of the rock-salt structure; it is not easy to examine them all. Annealing molecular dynamics (MD) calculations undertaken on the Kentuckia $AeTiO_2$, Ae = Ca, Sr, or Ba, structures (2000−100 K) did not alter the phase.

To our knowledge, there are no $AeTiO_2$ phases known. The reaction of $TiO_2$ with Ae metals (Ae = Mg, Ca, Sr, and Ba) at 950 °C for 7 days gave AeO, $AeTiO_3$, $Ae_2TiO_4$, $AeTi_4O_9$, TiO, and $Ti_2O$ phases but not the computed Kentuckia or rock-salt $AeTiO_2$ phases. The corresponding powder X-ray diffraction (pXRD) patterns (experimental and simulated) are shown in the SI. Perhaps a low-temperature synthetic method[3] provides a better pathway to the preparation of $AeTiO_2$.

Rock-salt or Kentuckia in structure, this would be an interesting set of compounds.

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**Supporting Information Available:** The computational methods summary, the band structures and DOS, the corresponding optimized structures with absolute energies, the experimental synthetic procedure, experimental and computational pXRD patterns, and phonon dispersion. This material is available free of charge via the Internet at http://pubs.acs.org.

## References

(1) Bucknum, M. J.; Castro, E. A. *Russ. J. Gen. Chem.* **2006**, *76*, 265.
(2) Siegrist, T.; Zahurak, S. M.; Murphy, D. W.; Roth, R. S. *Nature* **1988**, *334*, 231.
(3) Tsujimoto, Y.; Tassel, C.; Hayashi, N.; Watanabe, T.; Kageyama, H.; Yoshimura, K.; Takano, M.; Ceretti, M.; Ritter, C.; Paulus, W. *Nature* **2007**, *450*, 1062.
(4) Hoffmann, R. *Solids and Surfaces: A Chemist's View of Bonding in Extended Structures*; WILEY-VCH: New York, 1988.
(5) Burdett, J. K. *Chemical Bonding in Solids*; Oxford University Press: Oxford, UK, 1995.
(6) Banus, M. D.; Reed, T. B.; Strauss, A. *J. Phys. Rev. E* **1972**, *5*, 2775.
(7) Hughbanks, T.; Burdett, J. *J. Am. Chem. Soc.* **1984**, *106*, 3101.
(8) Baenziger, N. C.; Rundle, R. E. *Acta Crystallogr.* **1948**, *1*, 274.
(9) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*, 2nd ed.; Butterworths/Heinemann: Oxford, 1997; Chapter 22, pp 961−975.
(10) Kölle, U.; Kölle, P. *Angew. Chem., Int. Ed.* **2003**, *42*, 4540.
(11) Meagher, E. P.; Lager, G. A. *Can. Mineral.* **1979**, *17*, 77.
(12) Horn, M.; Schwerdtfeger, C. F.; Meagher, E. P. *J. Am. Ceram. Soc.* **1970**, *53*, 124.
(13) Glass, C. W.; Oganov, A. R.; Hansen, N. *Comput. Phys. Commun.* **2006**, *175*, 713.
(14) Oganov, A. R.; Glass, C. W. *J. Chem. Phys.* **2006**, *124*, 244704.
(15) Oganov, A. R.; Glass, C. W; Ono, S. *Earth Planet Sci. Lett.* **2006**, *241*, 95.

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