

3.014 Materials Laboratory  
Fall 2006

## **LABORATORY 2: Module $\beta_1$**

### *Radius Ratios and Symmetry in Ionic Crystals*

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#### **Objectives**

Discover principles of X-ray diffraction from crystalline materials  
Collect X-ray powder diffraction patterns and analyze using Powder Diffraction File (PDF)  
Explore relationship between relative ion sizes and crystal structure symmetries

#### **Tasks**

Calculate structure factors of materials investigated  
Prepare samples for X-ray powder diffraction  
Obtain X-ray powder diffraction patterns for 4-5 perovskite-structure oxides  
Compare patterns obtained to calculations and PDF  
Apply peak fitting routines to determine lattice parameters  
Relate composition, lattice parameter, ionic radius, radius ratio, and crystal symmetry

#### **Materials**

CaTiO<sub>3</sub>, BaTiO<sub>3</sub>, SrTiO<sub>3</sub>, PbTiO<sub>3</sub>, CaZrO<sub>3</sub>, PbZrO<sub>3</sub>

#### *Introduction*

Many inorganic materials, such as halides like NaCl and oxides like MgO, TiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub>, exhibit strong ionic character in their atomic bonding. As a result, atom packing in these systems is dictated by electrostatic forces—the structures chosen by nature are those that maximize interactions between ions of opposite charge while minimizing contact between like-charged ions and maintaining electrical neutrality. Structural consideration of ionic solids begins with the Goldschmidt<sup>1</sup> ionic model, which assumes that ions are essentially charged, incompressible, non-polarizable spheres with a definable radius. As a consequence of electrostatic interactions, ionic crystals create ordered arrangements of coordination polyhedra, in which cations are in contact with a maximum number of surrounding anions, the number depending on the ratio of the cation radius to the anion radius,  $r_C/r_A$  (Table 1), and to a lesser extent cation charge. A large

highly charged cation (such as  $\text{Ba}^{2+}$  or  $\text{U}^{4+}$ ) can accommodate a larger number of anions around it.  $\text{U}^{4+}$  cations in  $\text{UO}_2$  are 8-coordinated by  $\text{O}^{2-}$  anions in the fluorite structure

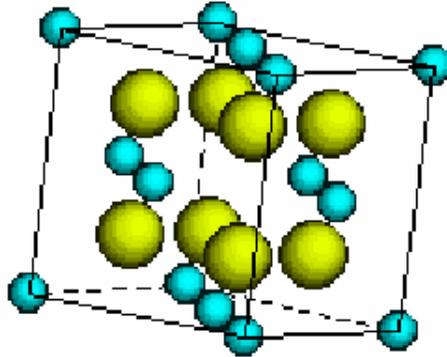


Fig. 1. (8:4) Fluorite structure of  $\text{UO}_2$ , with  $r_C/r_A$  ratio = 0.724. The  $\text{U}^{4+}$  cations form a cubic face-centered arrangement, but alternatively can be thought of as filling *every other* cube interstice in the simple cubic arrangement of  $\text{O}^{2-}$  anions, or as  $[\text{UO}_8]$  coordination cubes linked by sharing edges. In the (4:8) anti-fluorite structure of  $\text{Na}_2\text{O}$ , the roles of anion and cation are reversed, with  $r_A/r_C = 0.697$ ,  $\text{Na}^{2+}$  cations are four-coordinated to  $\text{O}^{2-}$  anions, and  $[\text{ONa}_8]$  cubes sharing edges.

(Fig. 1), while  $\text{Ba}^{2+}$  cations in perovskite-structure  $\text{BaTiO}_3$  (Fig. 5, see below) are 12-coordinated by  $\text{O}^{2-}$  anions). Conversely, smaller and less-highly charged cations cannot accommodate so many anions around them ( $\text{Li}_2\text{O}$  and  $\text{Na}_2\text{O}$  adopt the anti-fluorite structure (Fig. 1) in which the  $\text{Li}^{1+}$  and  $\text{Na}^{1+}$  cations are 4-coordinated by oxygen).

Table 1. Preferred Cation Coordination in Ionic Crystals

Cation Coordination No.	Anion arrangement	Minimum stable $r_C/r_A$
8	corners of cube	0.732
6	corners of octahedron	0.414
4	corners of tetrahedron	0.225
3	corners of triangle	0.155
2	co-linear	0

Of course, the anion point of view may equally be adopted. In the Na<sub>2</sub>O example just mentioned, eight (small) Na<sup>1+</sup> cations surround each (larger) O<sup>2-</sup> anion. In some cases (like BaO), the cation could accommodate a larger number of anions around it (e.g. 8 or 12) than the 6 it has, but the anion cannot accommodate around itself the geometrically consequential number of cations dictated by stoichiometry.

Table 2. *Coordination-Dependent Ionic Radii (Shannon & Prewitt<sup>3</sup>)*

Ion	Radius $r$ (pm) CN = 12	Radius $r$ (pm) CN = 8	Radius $r$ (pm) CN = 6	Radius $r$ (pm) CN = 4
Li <sup>1+</sup>			76	59
Na <sup>1+</sup>		118	102	99
K <sup>1+</sup>	185		138	
Rb <sup>1+</sup>		161	152	
Cs <sup>1+</sup>		177	167	
F <sup>1-</sup>		135	133	
Cl <sup>1-</sup>		184	181	
Mg <sup>2+</sup>			72	
Ca <sup>2+</sup>	134	112	100	
Sr <sup>2+</sup>	144	126	118	
Pb <sup>2+</sup>	149	129	119	
Ba <sup>2+</sup>	161	142	135	
Ti <sup>4+</sup>			61	
Nb <sup>5+</sup>			64	
Zr <sup>4+</sup>			72	
O <sup>2-</sup>		142	140	138

Ionic radii were first computed by the crystal chemist and Nobelist Linus Pauling<sup>2</sup> (also of X-ray crystallography and Vitamin C fame), but revised radii that take into account polarization of the ion cores, and thus depend on coordination, were calculated

more recently by Shannon and Prewitt <sup>3</sup> and are those now generally used (Table 2). Some of the stablest, and therefore most pervasive, ionic structures are those in which radius-ratio criteria are well satisfied for both anions and cations. Classic examples are those binary equiatomic compounds that crystallize in the rocksalt (halite) structure (Fig. 2b)—among them NaCl, KCl, LiF, KBr, CaO, SrO, BaO, CdO, VO, Fe<sub>1-x</sub>O, CoO, NiO, *etc.*—which have cation-anion radius ratios  $r_C/r_A$  near 0.5 (NaCl 0.563, MgO 0.514) and comprise cation (or anion) coordination octahedral (*e.g.* [NaCl<sub>6</sub>] octahedral) which share edges. For more similar ion sizes, the CsCl structure is preferred (CsCl itself has  $r_C/r_A = 0.96$ ) in which Cs<sup>1+</sup> ions sit in the centers of cubes of Cl<sup>-</sup> ions ([CsCl<sub>8</sub>] cubes) that share faces (Fig. 2).

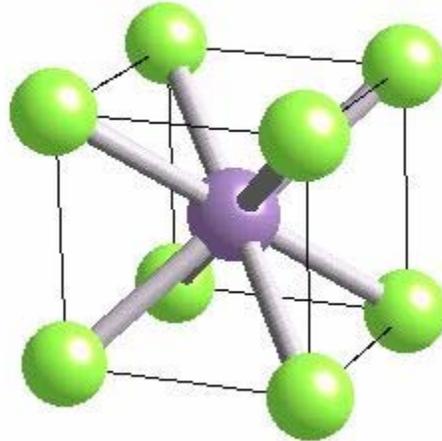


Fig. 2. (8:8) structure of CsCl, in which each ion is 8-coordinated by ions of the opposite charge, may also be thought of as [CsCl<sub>8</sub>] coordination cubes that share all faces.

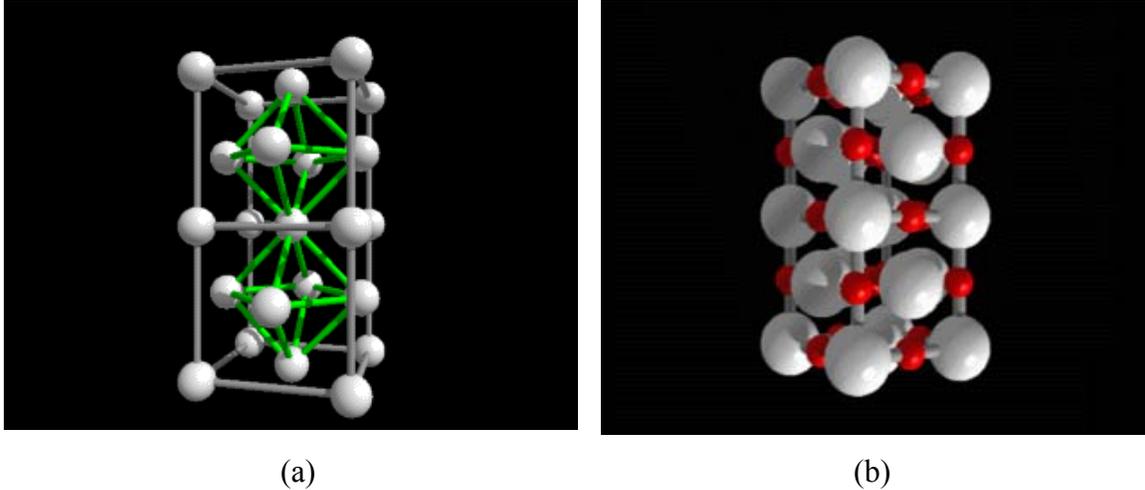
Linus Pauling's rules for crystalline compounds (Table 3) codify these notions and provide rationalization for structural tendencies observed in systems with ionic bonding. Despite being couched in terms of ion size, these rules turn out to be essentially driven more by the consideration of minimizing electrostatic energy (which can be accounted in a proper Madelung summation), than by the geometric necessities of ionic radii, however represented

Table 3. *Pauling's Rules for Crystalline Ionic Compounds*

<p><b>Rule 1. Coordination.</b> A coordination polyhedron of anions is formed around every cation (and <i>vice versa</i>) and is stable <i>only if the cation is in contact with each of its neighboring anions</i>. The distance between anions and cations is thus the sum of the their ionic radii, and the coordination number of the cation will be maximized subject to the criterion of maintaining cation-anion contact.</p>
<p><b>Rule 2. Electrostatic Valency.</b> The total strength of valency “bonds” that reach an anion from all of its neighboring cations equals the charge of the anion.</p>
<p><b>Rule 3. Polyhedral Linking.</b> Cation coordination polyhedra tend to be linked through sharing of anions, at corners first, then edges, then faces—in this order because of the electrostatic repulsion between cations.</p>
<p><b>Rule 4. Cation Evasion.</b> The electrostatic repulsion between cations is greatest for cations of high charge and small coordination number. Thus, in crystals containing different cations, those with higher charge and smaller coordination number are likely to share fewer polyhedral elements.</p>
<p><b>Rule 5. Crystal Homogeneity.</b> The number of structurally distinct sites in a crystalline arrangement of ions tends to be small. This condition ensures that chemically similar atoms experience similar environments</p>

In fact, ionic radii and radius ratios do *not*, in actuality, do a very good job at all in predicting the structure adopted by a given compound, even in such simple binary compounds as alkali halides, for which Table 1 would predict (4:4) zincblende structure for  $0.225 < r_C/r_A < 0.414$ , (6:6) rocksalt structure for  $0.414 < r_C/r_A < 0.732$ , and (8:8) CsCl structure for  $1 > r_C/r_A > 0.732$ . In actuality, LiF ( $r_C^{IV}/r_A^{IV} = 0.451$ ) only just escapes zincblende structure (the  $\text{Li}^{1+}$  ion does almost rattle around in its cage of six  $\text{F}^{1-}$  ions), but LiBr ( $r_C^{VI}/r_A^{VI} = 0.388$ ) and LiI ( $r_C^{VI}/r_A^{VI} = 0.345$ ), which also adopt the rocksalt structure, are incorrectly predicted as zincblende. NaF ( $r_C^{VI}/r_A^{VI} = 0.767$ ), KF ( $r_C^{VI}/r_A^{VI} = 1.038$ ), RbF ( $r_C^{VI}/r_A^{VI} = 1.128$ ), and CsF ( $r_C^{VI}/r_A^{VI} = 1.256$ ), all of which adopt the rocksalt structure, are likewise incorrectly predicted as CsCl. Ionic radii and radius ratios must therefore be used with care in understanding compound structures.

Often ionic crystals can be alternatively described as a close packed lattice of anions into which cations are placed on interstitial sites (Fig. 3a). In this description of the rocksalt structure of MgO,  $\text{Mg}^{2+}$  cations occupy every octahedral interstice in a cubic close-packed array of  $\text{O}^{2-}$  anions. The corundum structure adopted by  $\alpha\text{-Al}_2\text{O}_3$ , consists



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Fig. 3. (a) Octahedral cages (green) surrounding octahedral interstitial sites in a cubic close-packed array of anions. (b) Placement of  $\text{Mg}^{2+}$  cations (red) in every octahedral interstice of a close-packed array of  $\text{O}^{2-}$  anions to form the rocksalt structure adopted by the compound MgO. Images from <http://www.uncp.edu/home/mcclurem/lattice/>

of a (nearly) close-packed hexagonal assembly of  $\text{O}^{2-}$  anions, two-thirds of the octahedral interstices of which are occupied by  $\text{Al}^{3+}$  cations. In magnetite,  $\text{Fe}_3\text{O}_4$ , which adopts the (inverse) spinel structure,  $\text{Fe}^{3+}$  cations occupy 1/8 of the tetrahedral interstices and  $\text{Fe}^{2+}$  cations 1/2 the octahedral in a cubic close-packed array of  $\text{O}^{2-}$  anions. Perovskite compounds—the subject of this laboratory experiment, with chemical formulae of the form  $\text{ABO}_3$ —can be thought of as a cubic close-packed array of  $\text{O}^{2-}$  anions in which 1/3 of the octahedral interstices are occupied by A cations and 1/6 of the tetrahedral interstices by B cations. Pauling’s first rule still applies here, in that the cation placed in an interstitial site must not “rattle” around in the interstitial space if it is to stabilize the crystal structure.

The crystalline mineral perovskite ( $\text{CaTiO}_3$ ), from which the associated structural class takes its name, was discovered in the Russian Ural Mountains by Gustav Rose in 1839 and named for the Russian mineralogist L. A. Perovski (1792-1856). A more

illuminating description of the idealized perovskite structure involves linking of Pauling's coordination polyhedra (Fig. 4b) in accordance with Pauling's rules.  $[\text{TiO}_6]$  octahedra

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Fig. 4. Two representations of the perovskite structure. a,b) Ti-centered representation of  $\text{BaTiO}_3$ , showing uniaxial displacement of undersized  $\text{Ti}^{4+}$  cation in the tetragonal variant below the Curie temperature in a) and the average cubic ideal structure above the Curie temperature in b). c) Ca (blue)-centered representation of  $\text{CaZrO}_3$ , showing linkage of  $[\text{ZrO}_6]$  coordination octahedra (yellow) through corner sharing of oxygen anions (red). The tilting of the  $[\text{ZrO}_6]$  octahedra is typical of non-ideal perovskites with tolerance parameter  $0.9 < t < 1.0$ . (Reproduced from W. D. Kingery et al., ref. 5).

comprising small, highly-charged  $\text{Ti}^{4+}$  cations surrounded by 6  $\text{O}^{2-}$  anions share only corners (unlike  $[\text{MgO}_6]$  octahedral in the rocksalt structure, comprising larger, less highly charged  $\text{Mg}^{2+}$  cations, which share edges), in keeping with Pauling's third rule, in a cubic arrangement. In this configuration,  $\text{O}^{2-}$  anions thus share valency "bonds" with two  $\text{Ti}^{4+}$  cations. The arrangement also defines a large interstitial space which can be occupied by a large cation of lower charge, in this case  $\text{Ca}^{2+}$ , which is 12-coordinated by  $\text{O}^{2-}$  anions in  $[\text{CaO}_{12}]$  truncated cubes that share square faces with each other and triangular faces with the  $[\text{TiO}_6]$  octahedral, as allowed by Pauling's fourth rule.  $\text{O}^{2-}$  anions thus additionally share valency "bonds" with four  $\text{Ca}^{2+}$  cations, satisfying Pauling's second rule (the two  $\text{Ti}^{4+}$  cations each contribute  $2 \times 4/6 = 16/12$  "valency bonds" and the four  $\text{Ca}^{2+}$  cations  $4 \times 2/12 = 8/12$  "valency bonds" to each  $\text{O}^{2-}$  anion, for a total of  $24/12 = 2$  "bonds," which equals the ionic charge  $|-2| = 2$  of the  $\text{O}^{2-}$  anions). The fact that the ideal crystal

structure of perovskite, in fact, satisfies Pauling’s Rules rather well implies substantially ionic character to the bonding—although it is known that the Ti-O bond has significant covalency and Ti is 6-coordinated by O because this maximizes covalent bonding, not because the ionic radius-ratio  $r_{\text{Ti}^{4+}}/r_{\text{O}^{2-}} = 75 \text{ pm}/126 \text{ pm} = 0.60$  (in  $\text{TiO}_2$ ) is consistent with octahedral ionic coordination.

The perovskite structure is adopted by a large number of other  $\text{A}^{2+}\text{B}^{4+}\text{O}_3$  compounds, among them (besides  $\text{CaTiO}_3$ )  $\text{SrTiO}_3$ ,  $\text{BaTiO}_3$ ,  $\text{PbTiO}_3$ ,  $\text{PbZrO}_3$  and  $\text{CaZrO}_3$ , which you will study, and additionally compounds such as  $\text{KNbO}_3$  in which a large  $\text{K}^{1+}$  cation is charge-compensated by a small  $\text{Nb}^{5+}$  cation. The radius-ratio criterion (Pauling’s first rule) is, however, precisely satisfied only by  $\text{SrTiO}_3$  (which is cubic); other combinations of A and B cations do not ensure that the cations are in “contact” with  $\text{O}^{2-}$  anions. Geometrical contact of hard ion spheres occurs only if  $(r_{\text{A}} + r_{\text{O}}) = \sqrt{2}(r_{\text{B}} + r_{\text{O}})$ . A structural tolerance parameter<sup>4</sup> can be thus defined

$$t = (r_{\text{A}} + r_{\text{O}})/\sqrt{2}(r_{\text{B}} + r_{\text{O}}) \quad (1)$$

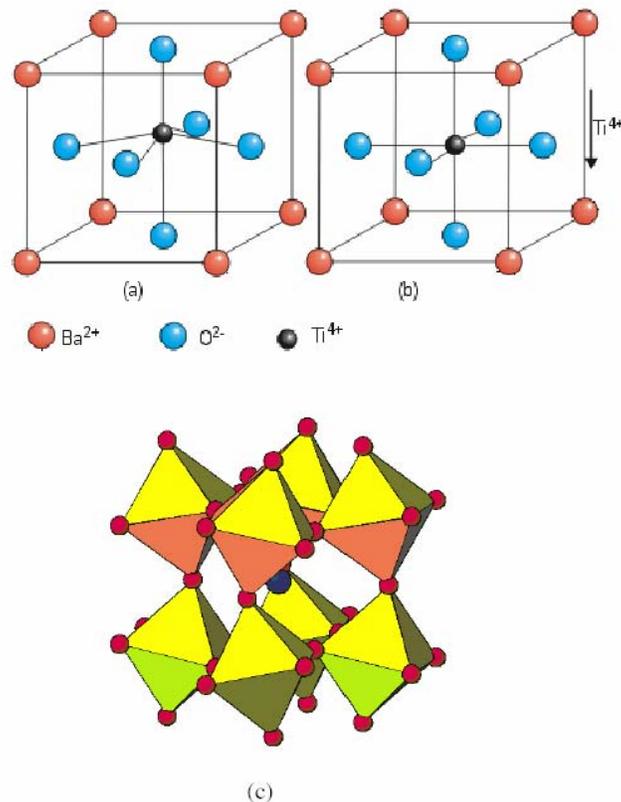
that defines the limits of 6-fold and 12-fold coordination for the B and A cations in this structure type, and the perovskite structure type is stable generally only within the range

Table 4. *Tolerance Parameter for Perovskite Structure Compounds*

$\text{CaZrO}_3$	$\text{CaTiO}_3$	$\text{PbZrO}_3$	$\text{SrTiO}_3$	$\text{PbTiO}_3$	$\text{BaTiO}_3$	$\text{KNbO}_3$
0.914	0.964	0.964	0.999	1.017	1.059	1.127

$0.75 < t < 1.10$  (Table 4). For  $t < 0.90$ , a cooperative buckling of the corner-sharing octahedra occurs that increases the lattice parameter. For  $0.90 < t < 1$ , small distortions or rotations of the octahedra occur (Fig. 4c) that provide cation-anion “contact” but lower the crystal symmetry from cubic to orthorhombic. For  $t > 1$ , highly correlated uniaxial displacements of the B cations occur (Fig. 5a) that convert the cubic symmetry to tetragonal symmetry by selective elongation of one axis. Presence of these distortions, rotations or displacements is easily distinguished by the appearance in diffraction patterns

of diffraction maxima that are forbidden (have zero structure factor, see below) for the cubic structure and the splitting of certain diffraction peaks (*e.g.* those of the family  $\{h00\}$ ) that would have arisen from crystallographically equivalent planes in the cubic system. They are also responsible for an intriguing array of unusual electrical properties (ferroelectricity, piezoelectricity [BaTiO<sub>3</sub>, Pb(Zr,Ti)O<sub>3</sub>], electrostriction [Pb(Mg,Nb)O<sub>3</sub>, fast ion conduction [LaMnO<sub>3</sub>]) and magnetic properties (magnetoresistance [(La,Ca)MnO<sub>3</sub>, (La,Sr)CoO<sub>3</sub>]). The cubic→tetragonal transformation temperature corresponds to the Curie temperature, below which ferroelectric behavior appears.



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Fig. 5. Distortions of the perovskite structure accompanying departures from ideality in ion radius ratio. a) Highly correlated uniaxial displacements of undersized Ti<sup>4+</sup> cation that result in a tetragonal variant of BaTiO<sub>3</sub> ( $t = 1.059$ ), stable below the Curie temperature but reverting to b) an average-cubic ideal structure above the Curie temperature when the directions of the displacement become uncorrelated. c) Tilting of the [ZrO<sub>6</sub>] octahedra in CaZrO<sub>3</sub> ( $t = 0.914$ ), typical of non-ideal perovskites with overlarge B cations and tolerance parameters  $0.9 < t < 1.0$ , that results in orthorhombic symmetry.

Even in SrTiO<sub>3</sub>, the ideal cubic perovskite arrangement is stable as a sort of “average” structure only above –55° C. Below that critical temperature, SrTiO<sub>3</sub> undergoes a tetragonal distortion, like that of room-temperature BaTiO<sub>3</sub> and PbTiO<sub>3</sub>, whose own cubic→tetragonal transformation temperatures are 130° C and 490 °C, respectively.

### References

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