Ceramic Materials and Multilayer Electronic Devices

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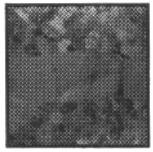

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Proceedings of the High Strain Piezoelectric Materials, Devices, and Applications and Advanced Dielectric Materials and Multilayer Electronic Devices Symposia held at the 105th Annual Meeting of the American Ceramic Society, April 27–30, 2003 in Nashville, Tennessee.

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COVER PHOTO: "Structure of multilayer ceramic capacitor" is courtesy of Yoshinori Fujikawa, Fumikazu Yamane, Takeshi Nomura, and Yasuyuki Kitano and appears as figure 1 in their paper "Characterization of $BaTiO_3$ Powders by Transmission Electron Microscopy and Scanning Transmission Electron Microscopy," which begins on page 115.

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Preface

The growth of materials research, development of technology, and product innovation has been extraordinary during the last century. Our understanding of science and technology behind dielectric materials played a major role in satisfying the social needs by developing electronic devices for automotive, telecommunications and medical applications. Dielectric technology development still has an enormous potential role to play in developing future materials for electronic applications. We will continue our growth efforts during this century to satisfy the increased demands of our society.

Materials societies like The American Ceramic Society (ACerS) understand their social responsibility. For the last many years, ACerS has organized several international symposia covering many aspects of the advanced electronic materials systems by bringing together leading researchers and practitioners of electronics and publishing proceedings of the conferences in the Ceramic Transaction series.

This volume contains a collection of selected papers from two symposia: Advanced Dielectric Materials and Multilayer Electronic Devices and High Strain Piezoelectric Materials, Devices and Applications that were held during the 105th Annual Meeting of The American Ceramic Society, April 27-30, 2003, Nashville, Tennessee. Major topics of the symposium were: fundamental and historical perspectives of dielectric materials; relaxor materials and devices; high strain piezoelectric devices; advanced aspects of powder preparation, characterization and properties; thin films; materials for low and high frequency applications; processing-structure-property-relationships; and potential areas of applications. Over fourteen invited and twenty-five contributed papers are peer-reviewed and included in this volume.

We, the editors, acknowledge and appreciate the contributions of the speakers, conference and session chairs, manuscript reviewers, and the ACerS staff for making this endeavor a successful one.

Finally, we dedicate this volume to the memory of professor W. D. Kingery and his contributions to modern ceramics.

K. M. Nair,
A.S. Bhalla
S-I. Hirano
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Design and Preparation of Materials

THE ROLE OF CRYSTAL CHEMISTRY IN THE DESIGN OF DIELECTRIC MATERIALS

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ABSTRACT

To a surprisingly accurate approximation, the crystal structure of a compound depends only on electrostatic forces holding ions together. On the order of 95% of the lattice energy can be ascribed to Coulomb forces. As a result, ions with the same size and charge can often be substituted interchangeably. A relatively small number of primary structures, with their distorted, ordered, and superstructure variants, account for a very large number of compounds. Phase transitions, structural and electronic ordering, and domain structures represent only a very small percentage of the total lattice energy but can sometimes be addressed by crystal chemical mapping.

INTRODUCTION

Crystal chemistry is concerned above all with the systematics of crystal structures. Although the emphasis is on structure, crystal chemistry is not crystallography. Crystal structures determined by the methods of x-ray, neutron, and electron diffraction are only the feedstock from which crystal chemical principles are sorted out.

When the experimental methods and underlying theory for extracting crystal structures from diffraction patterns were worked out in the early years of the 20th Century, there followed an outpouring of structure determinations. It was quickly recognized that some sets of compounds with quite different chemical composition had the same atomic arrangement. Thus NaCl, MgO, and MnS all have the same cation and anion positions within a face-centered cubic unit cell. The cell constants are different but these only serve to scale otherwise identical crystal structures. By the early 1920's a sufficient library of crystal structures had been built up that it was possible to search for systematic patterns. Crystal chemistry had been born.

The guiding principles are empirical. The concept of a structure type and the systematic organization of crystal structures was proposed by Goldschmidt[1] in 1926. There are Pauling's rules[2] which first appeared in 1929. By 1933 Neuburger[3] could write a full treatise on the principles of crystal chemistry and by 1939, Evan[4] had published the first edition of his classic textbook.

Because the roots of crystal chemistry go so deep into the past, the subject sometimes has a musty smell, as though it is a relict that should have long since been superceded by the modern theory of chemical bonding. What is important is that the broad empirical principles of crystal chemistry remain as valid today as they were 80 years ago. And even more importantly, they remain useful as a practical guide to materials design. At a certain level, the back-of-the-envelope principles of crystal chemistry can compete with the elegant molecular orbital and band theoretical calculations that are now used to rationalize molecular and crystal structures.

PRINCIPLES OF CRYSTAL CHEMISTRY

Packing Principles

The fundamental premise of crystal chemistry is that ions can be treated as charged spheres that are then held together by electrostatic forces. An assemblage of ions will arrange themselves to minimize the potential energy. Rather than details of chemical bonding, many of the primary features of crystal structures are a matter of pure geometry. Anions are usually larger than cations so it is convenient to examine the ways in which large spheres can be packed around smaller ones. The arrangements are most stable when all ions just touch. This provides the best balance between Coulomb attraction and the onset of the repulsion forces. If the central cation is too small, anion-anion repulsion will destabilize the structure, anions will be rejected, and a new arrangement with fewer anions will appear. If the central cation is too large, the anions will be spread out and Coulomb attraction will pull in additional anions. The controlling variable is the ratio of cation radius to anion radius, not the absolute values of the radii.

The number of anions that can pack around a cation is the *coordination number*. The clusters consisting of a central cation and its coordinating anions form coordination polyhedra. Because of anion-anion repulsion, the coordination polyhedra take regular forms of triangles, tetrahedra, octahedra and cubes. If the most stable polyhedra are those in which the cation and anions just touch, simple geometry gives the ideal radius ratios (Table I). Of course, not all combinations of ions will produce ideal radius ratios. The interionic repulsion forces increase as the 8 – 9 power of the interatomic distances (or exponentially depending on the potential function used) and rapidly destabilize the polyhedra for radius ratios smaller than the ideal value. For ratios higher than the ideal value the destabilization depends on the Coulomb attractive force which varies slowly with distance. Thus the stability interval ranges from the ideal ratio up to the ratio of the next higher coordination number.

Multicomponent Systems

The concepts of coordination polyhedra and sphere packings assumed that there were only two sizes of spheres – large anions and small cations. This is appropriate for binary compounds. In systems with larger numbers of components there will be the possibility of more than one kind of coordination polyhedron and a competition among the cations as to which fits into which. Cations may have different charges and this will affect the distribution of cations among available polyhedra.

A master principle in any structural arrangement is that of charge neutrality. It is essential that positive and negative charges balance and further that they do so over short distances within the structure. An unyielding guideline in distributing ions within crystal structures is that local charge balance must be maintained.

Table I. Radius ratios for coordination polyhedra

Coordination No.	Radius Ratio	Configuration	Example
2	0 – 0.155	Linear	CO_2
3	0.155 – 0.224	Planar Triangle	CO_3^{2-}
4	0.224 – 0.414	Tetrahedron	SiO_2
4	0.414 – 0.732	Planar Square	CuO
6	0.414 – 0.732	Octahedron	MgO
8	0.732 – 1.0	Cube	CaF_2

Linkages

Although many structures can be considered examples of the closest packing of spheres, many other structures are more loosely packed and can best be described in terms of the coordination polyhedra and the ways in which the polyhedra can be linked to form continuous structures. The silicates are the most common example. The structural building block (at ambient pressures) is the SiO_4 tetrahedron. However, the tetrahedra can be linked in a great variety of dimers, chains, rings, sheets, and three-dimensional frameworks if one considers only the possibilities within corner-sharing.

Polyhedra can appear as isolated units, with shared corners, with shared edges, and with shared faces. As noted by Pauling long ago, shared edges, and more significantly shared faces, tends to destabilize the polyhedra. An examination of a many crystal structures reveals the trends shown in Table II. The concept of structural buildup from coordination polyhedra works for both closed packed and non-close-packed structures. Structures built of close-packed spheres also contain close-packed polyhedra.

Table II. Trends in polyhedral linkages

	Tetrahedra	Octahedra	Cubes
Isolated Units	Common	Occasionally	Extremely Rare
Corner-Sharing	Common	Common	Rare
Edge-Sharing	Very Rare	Common	Common
Face-Sharing	Never	Rare	Common

A Summary of Principles

(1) Crystals are composed of cations and anions, each treated as spheres with a specified charge and radius.

(2) Sphere packing is controlled by the balance between attractive and repulsive electrostatic forces and leads to polyhedra of various geometries depending essentially on the ratio of cation radius to anion radius, not the absolute values of these parameters.

(3) Charge balance must be maintained over short distance scales.

(4) Because ion size and charge are the key parameters, ions of similar size and charge are largely interchangeable regardless of their chemistry.

(5) Because of principle (4), the number of essentially different kinds of structural constituents in a crystal tends to be small (Pauling's fifth rule; also called the "rule of parsimony"). Likewise, the number of essentially different crystal structures is much smaller than the number of compounds that take those structures.

CHEMICAL BONDING

The Ionic Bond: Electrostatic Models

Solid materials represent a great variety of chemical bonding. There are halides and oxides which are close to ideal ionic solids, there are polymers and organic compounds made of covalently bonded molecules held together in the solid by van der Waals or hydrogen bonding, there are metals, there are semiconductors with both metallic and covalent character, there are silicates, phosphates, and carbonates with mixed covalent and ionic character within the same compound. Traditionally, the strong bonds were characterized as ionic, covalent, and metallic. Each is based on a different conceptual framework and each has a different theoretical structure. As suggested in Fig 1, many classes of materials are not ideally described by any of the models.

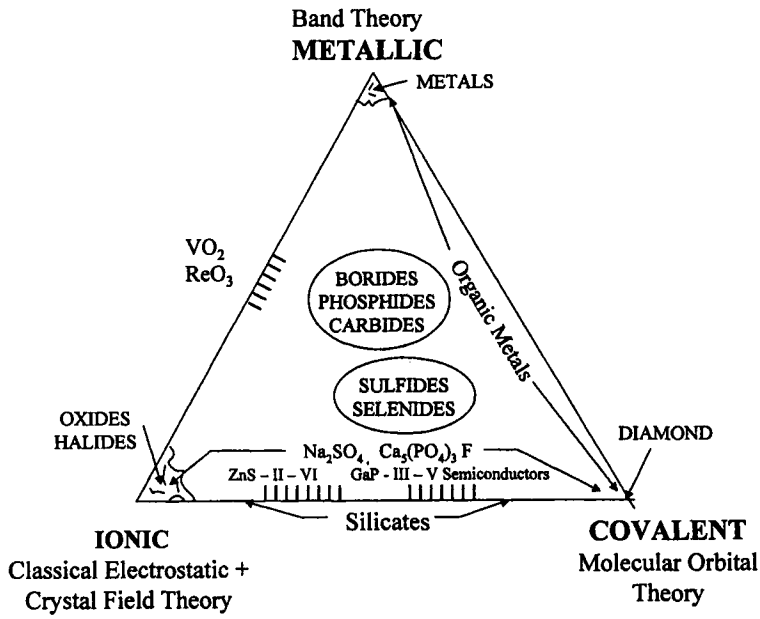

Figure 1: The three types of strong chemical bonds with corresponding theoretical model. Typical compounds with various pure and mixed bond types are illustrated.

The ionic model is based on classical electrostatic forces between charged ions. The attractive force pulling ions together is a Coulomb force that increases slowly with the inverse of the distance between the ions. When ions approach each other to a distance where the outer electron shells begin to overlap, there is a short-range repulsive force that increases very rapidly as the interatomic distance decreases further. The balance between attractive and repulsive forces defines the equilibrium interatomic distance and is expressed by a potential function of the form

$$V = -\frac{e^2 z_+ z_- A}{r} + Be^{-\frac{r}{\rho}}$$

Several expressions have been used for the repulsive potential. The one given here is the Born potential. Although there is some quantum mechanical justification for this function, the parameter, ρ, is generally taken as an empirical parameter with a numerical value of 0.345. It should be noted that as a theory of the chemical bond, the electrostatic model doesn't actually display any bonds. The electrons remain localized on their parent ions, the electrostatic fields are

spherically distributed, and the charge density between the ions trends toward zero.

The potential function applies to individual ion pairs. By fixing r = equilibrium distance and multiplying by the number of ion pairs per mole of material, N_0, equation (1) leads immediately to the lattice energy, U.

$$U = -\frac{e^2 z_+ z_- A N_0}{r_{equil}}\left(1 - \frac{\rho}{r_{equil}}\right)$$

In these equations, e is the charge on the electron, z_+ and z_- are the formal charges on the cation and the anion respectively, and A is known as the Madelung constant. The repulsive force acts only over short distances and varies little with next nearest neighbors. However, the Coulomb attractive forces varies slowly with distance and thus for a target cation, the attraction by nearest neighbor anions, repulsion by next nearest neighbor cations, more attraction by next-next-nearest neighbor anions and so on, gives rise to a long series of terms which converges only slowly. The sum of the series is the Madelung constant, A. The Madelung constant is a dimensionless parameter determined only by the arrangement of the ions and not by their actual interatomic distances. As a result, each crystal structure type has its own unique value of the Madelung constant.

In spite of its theoretical simplicity and classical forces, the ionic model works remarkably well. Calculated lattice energies are usually within five percent of measured values. The modern reincarnation of the electrostatic model is in molecular dynamics. These calculations use potential functions not very different from those described above.

The main problem with the classical electrostatic model as a theory of the solid state is that equation (2) gives only the ground state of the system. There is no provision for excited states and no provision for any sort of transport properties. To some extent, these limitations can be overcome by superimposing crystal field theory[5] on the simple ionic model. Crystal field theory assumes a fixed and pre-determined anion arrangement which provides an electrostatic field that interacts with the orbital states of d- and f-electrons of the cations. The resulting energy levels are determined by the symmetry of the crystallographic site occupied by the transition metal or rare earth ion, and by the interatomic distances. Although crystal field energy levels are in principle determined by d-orbital and f-orbital wave functions, the calculations are compacted into a few empirically derived parameters so that crystal field theory is very useful in describing magnetic properties, color, and luminescence of ionic compounds. The contribution of crystal field energies to the overall lattice energy is small but sufficient to account for unusual crystal chemical behavior in ions such as Cr^{3+} and Ni^{2+}.

The Covalent Bond: Molecular Orbital Models

The conceptual picture of molecules is that they are arrays of atoms held together by bonds. The molecular orbital model describes the bonds as being built up from mixtures of the atomic orbitals derived from the atoms being bonded. One must assume a structure and estimate interatomic distances. The orbital combinations are in large part determined by the symmetry of the assumed structure because allowed combinations are required to transform properly under the operations of the molecular point group. Once the orbital structure is determined, the orbitals are populated with the available electrons drawn from all atomic orbitals outside the closed noble gas cores. The more orbitals and the more electrons that can be included, the more accurate the calculated energy levels. Early molecular orbital calculations were limited by available computing power and many simplifications had to be made. The current generation of molecular orbital models such as GAUSSIAN98 have large basis sets and can be used as working tools without too much concern for the internal mathematics. Many useful calculations can be made[6,7]. These programs are particularly useful for excited states, transient species, surface species and other molecular units where direct observation is difficult.

Molecules are intrinsically closed systems whereas crystals are not. Direct application of molecular orbital methods to the energy level structure and overall stability of crystalline solids required extracting clusters or fragments that are small enough to allow computation. By repeating the calculations for various combinations of crystallographic parameters, the combination that produces the minimum energy can be identified. Good results have been obtained for structures as complex as spinel and olivine[8].

The Metallic Bond: Band Models

Band theory was created in order to understand the electrical conductivity, thermal conductivity, and other properties of metals. The basic concept was that of an array of atomic cores, arranged according to the known crystal structure of the metal. The valence electrons, rather then being localized on any particular atom were treated as an electron gas, completely delocalized throughout the crystal structure. The wave functions for the valence electrons would all mix generating a number of states comparable to the number of atoms in the crystal. Because of the Pauli exclusion principle, there would remain closely spaced, but discrete energy states so that the overall energy levels would have spread to form bands from fractions of an electron volt to several electron volts wide. The guiding symmetry is the translational symmetry of the metal structure. Because electrons are delocalized, they also carry momentum. The results of band structure calculations are plotted as energy as a function of momentum along specified directions in the Brillouin zone.

Band theory is the most comprehensive of the various theories of the chemical bond. It can accommodate insulators and semiconductors and indeed metals become simply structures with partially filled bands. The main drawback of the band model is that it lacks the intuitive or interpretive aspects associated with the chemical bonds of molecular orbital theory and full calculations must be made for quantitative interpretation, something that is difficult for complex structures. However, in recent years, good success has been achieved in blending band concepts with both crystal chemistry and with more traditional views of the chemical bond[9,10]. There has been a convergence of the three models into hybrids that can be adapted to structures of interest.

STRUCTURE TYPES AND STRUCTURE FIELD MAPS

The reason why crystal chemistry remains an effective model for organizing and predicting crystal structures, in spite of the impressive improvements in theoretical models for the chemical bond, is that all of the theories produce potential functions of roughly the same shape (Fig. 2). Further, the central variable is the interatomic distance. So at the sophistication level of crystal chemistry's back-of-the-envelope calculations, the detailed theory of the chemical bond doesn't really matter all that much so long as some aspect of ionic character remains. It is possible to proceed with an organizational scheme that utilizes as variables only ionic radii, ionic charge, and to a lesser extent ionic polarizability and special electronic features of ions.

Binary Compounds

The structures of binary compounds consist mostly of arrangements of a single kind of cation coordinated by a single kind of anion. Because of the necessity of local charge neutrality, the possible arrangements of ions depends both on the ionic radii and charge and on proportions of the ions. Thus comparisons are made for structures with the same stoichiometry: AX, AX_2, A_2X_3, and any others of interest.

Examination of a very large number of compounds with the same stoichiometry reveals that they can be represented by only a small number of structure types. Many compounds will be isostructural which implies (i) same stoichiometry, properly defined, (ii) same relative atomic arrangement meaning same coordination numbers and same polyhedral linkages, and (iii) same space group. For each structure type, one compound is defined as a prototype. The choice of prototype is usually historical and certainly arbitrary. If the prototype occurs in nature, its mineral name makes a convenient label for the structure type. The advantage of the mineral name is that it implies both a composition and a structure. Thus we speak of the rutile structure (but not the TiO_2 structure), the calcite structure (but not the $CaCO_3$ structure), the spinel structure, the garnet structure, the perovskite structure and others. Something like 30 – 40 structure

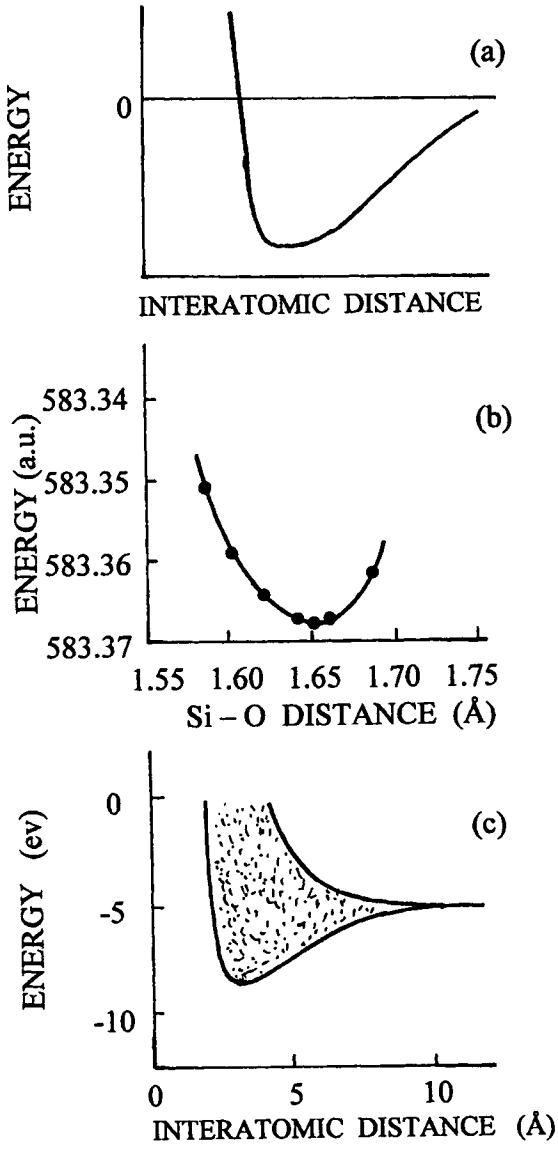

Figure 2: Potential functions for the three models of the chemical bond. A) Sketch of classic electrostatic potential. B) Potential function for SiO bond determined by earlier molecular orbital calulation[11] and C) 3s band of sodium.

types are sufficient to describe most of the compounds of interest to materials science. Some of the more important structure types for binary compounds are given in Table III.

For binary compounds, there are three primary plotting variables: anion/cation ratio, the cation radius, and the anion radius. If one holds the composition constant, all compounds with that composition can be plotted in terms of cation and anion radius. The result is known as a structure field map. A set of structure field maps for the AX composition are shown in Fig. 3 using Shannon-Prewitt crystal radii[12,13]. The anions have been separated into three groups by charge and the transition metal ions are also plotted separately. These maps demonstrate that ionic radii alone map the structures effectively but that the position of structure field boundaries also depends on charge. Note the trend in coordination numbers. As the anion charge is increased, lower coordination structures dominate. The 8-coordinated CsCl structure appears only among the

Table III. Some important binary structure types.

Structure	Prototype	Coordination No.	Space Group
AX			
Boron Nitride	BN	3	$P6_3/mmc$
Sphalerite	ZnS	4	$F\bar{4}3m$
Wurtzite	ZnS	4	$P6_3mc$
Halite	NaCl	6	Fm3m
Niccolite	NiAs	6	$P6_3mc$
CsCl	CsCl	8	Pm3m
AX_2			
Quartz	SiO_2	4	$P3_121$, $P3_221$
Rutile	TiO_2	6	$P4_2/mnm$
Brucite	$Mg(OH)_2$	6	$P\bar{3}m1$
Fluorite	CaF_2	8	Fm3m
Cotunnite	$PbCl_2$	9	Pnam
A_2X_3			
Corundum	Al_2O_3	6	$R\bar{3}c$
Bixbyite	Mn_2O_3	6	Ia3
A-Type	La_2O_3		$P\bar{3}m1$

halides. Note also the overlap between the 6-coordinated NiAs structure of the transition metal chalcogenides with the NaCl structure of the alkaline earth chalcogenides. This is indicative of the importance of the d-orbitals in certain

cases. The NiAs structure is composed of face-sharing octahedral which are stabilized by d-orbital overlap across the shared faces.

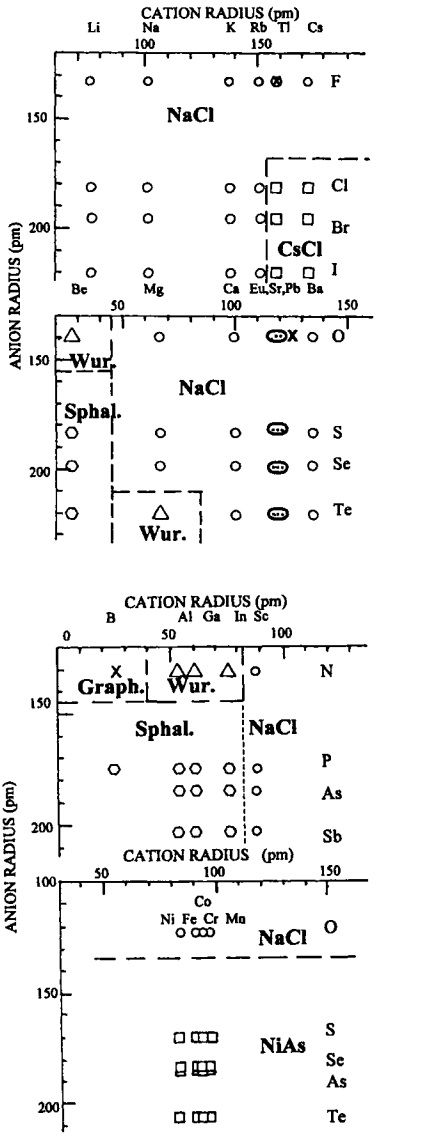

Figure 3: Structure field maps for AX compounds. The maps are arranged A^+X^-, $A2^+X2^-$, $A3^+X3^-$, and $M2^+X2^-$ where M is a divalent transition metal ion.

Building-Up Principles

Ternary compounds have two cations, Quaternary compounds have three cations and more complex compositions are possible. The requirement of local charge neutrality requires only that the sum of the cation charges equal the sum of the anion charges. This provides for a great variety of possible substitutions because charges on the cation sites can be mixed in different ways. Multiple substitutions mean that increasing the number of components does not lead to a great increase in the number of distinct structure types.

Some ternary structures are built up as compositional variations on basic binary structures; others are uniquely ternary. Figure 4 outlines the possibilities.

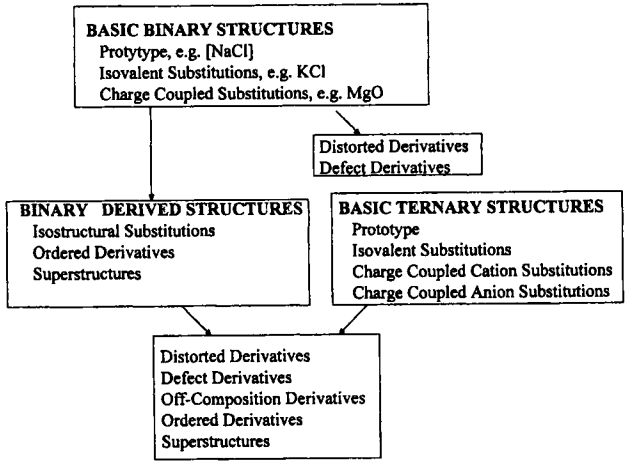

Figure 4: Schematic outline showing derivative structures of primary parent structures.

For each of the basic binary structures there is a defined prototype, for example NaCl. Most ions within the size constraints of the structure field can be substituted for Na^+ or Cl^- as isovalent substitutions. For many of these substitutions there will be complete solid solution so that partial substitution is also possible. Other families of isostructural compounds are formed by changing both cation and anion charge, as for example, replacing Na^+ by Mg^{2+} and at the same time replacing Cl^- by O^{2-}. These substitutions produce compounds that are strictly isostructural with the prototype. However, other closely related structures may occur as small distortions of the primary structures. VO_2 is monoclinic but is only slightly distorted from the rutile structure. In Fig. 3, TlF appears in the field of the NaCl structure but it has an orthorhombic distortion of the NaCl structure.

One can simply replace half of the ions of the binary compound randomly with a different isovalent ion to form a ternary compound but this does not form a ternary structure, only a solid solution (e.g. $NaKCl_2$). There are ternary

compounds belonging to binary structure types although the end members do not have the binary structure. $LiNdS_2$ is a disordered compound with the NaCl structure but is not a solid solution. In contrast, if the cations are inserted in an ordered way, a new ternary structure may be formed. $LiLuS_2$ is related to NaCl but Li^+ and Lu^{3+} are arranged in alternate cation positions. As a result, symmetry is lost, the structure is elongated along the diagonal of the NaCl unit cell and a trigonal ordered derivative structure results. In general, substitution of two ions of the same charge will produce a solid solution whereas substitution of pairs of ions of differing charge will result in an ordered derivative structure.

Superstructures are also ordered arrangement but ordered arrangements that require defining larger unit cells to accommodate the ordered ions. Usually a superstructure is built with unit cells composed of two or more cells of the parent structure stacked in an ordered array. For example, the chalcopyrite structure, prototype $CuFeS_2$, is composed of two cubic sphalerite cells stacked on top of each other to produce a tetragonal cell with roughly the same a-axis as the sphalerite cell but twice the c-axis. Superstructures are found with very long stacking sequences.

Primary ternary structures are those that have no immediate structural relationship with any of the primary binary structures. Usually, this means that there will be more than one cation site, often with different coordination numbers, polyhedral linkages or both. Once the ternary structures have been identified, the structural variants of distorted derivatives, defect and off-composition derivatives, ordered derivatives and superstructures can often be found.

Ternary and Higher Systems

Table IV summarizes some of the more important ternary structures. Much more detail may be found in Muller and Roy's book[14]. The structures are organized by chemical composition as with the binary structures. The convention is to list the larger cation (usually higher coordination number) as A and the smaller cation as B. Considering all possible ternary compositions, it is obvious that there are a large number of possible cation/cation and cation/anion ratios. Table IV is limited to the simpler ratios ABX_2, ABX_3, ABX_4, and A_2BX_4 (which keeping with the cation size convention must also include AB_2X_4).

Although there are useful materials that fall into most of the structures, some structure types are more important than others. Within the ABX_2 family certain of the chalcopyrite compounds are optical materials. Within the ABX_3 family, calcite and aragonite are geologically important. However, the perovskite structure and its many derivatives are the core of the entire field of dielectric materials. The ABX_4 family is something of a hodge-podge. There are many structures, not all of them listed, based on packings of tetrahedra with various sizes of large A-ion. The zircon structure appears in ceramic pigments and in speciality refractories. In contrast, the A_2BX_4 family includes many important structures. Olivine is a major mineral in the earths crust and mantle and its phase transitions in the deep mantle are of important in geophysics. Among the spinel

structure compounds are chromite refractories, aluminate optical materials, and ferrite magnetic materials. Spinel superstructures include the β-alumina family of fast ion conductors.

CRYSTAL CHEMISTRY OF DIELECTRIC MATERIALS

The title of this section is rather overly pretentious. Dielectric materials include substances from wax paper to $BaTiO_3$. The term is often used in a broad sense to include ferroelectrics, piezoelectrics, pyroelectrics and other electrically and optically interesting insulators. Included in this very large assemblage of materials would be organic salts (e.g. triglycine sulfate), ionic salts (e.g. potassium dihydrogen phosphate), and a variety of polymers as well as ceramic compounds that fit into crystal chemical categories. The discussion that follows is not only limited to ionic compounds, but is further restricted to compounds related to the perovskite structure. Within this limitation, however, are a very large variety of phenomena at many levels of structural subtlety. Although the perovskite structure allows for a long and complex catalog of derivative structures, a similar catalog could be prepared for most of the structures listed in Table IV.

A huge number of compounds take the perovskite or one of its derivative structures[15]. In addition to dielectric materials, transition metal perovskites have application as catalysts[16] and as fuel cell materials. The high temperature superconductors are also built on perovskite-like structural units[17,18].

Non-Spherical Ions

The dielectric behavior of materials is described by the dielectric permittivity, both the real part which describes the dielectric response and the imaginary part which describes the dielectric losses. The permittivity in turn is a function of the polarizability of the material. Polarizability is determined in part by the intrinsic polarizability of the ions and in part by dipoles within the structure.

If ions are to be regarded as charged spheres, their polarizability generally increases with ionic radius, larger ions being more polarizable than smaller ions[19]. Ba^{2+} is highly polarizable; Al^{3+} is not. Some ions receive additional contributions to the polarizability from d-electrons and from non-bonding lone pair electrons.

Ions with filled d-shells, Zn^{2+}, Cd^{2+}, and Ga^{3+} for example, tend to occur in 4-fold coordination when their ionic radii would predict 6-fold coordination. Mixing of metal d-orbitals with ligand p-orbitals enhances a tendency to covalent bonding and the greater polarizability of the shared electron bond.

Certain ions, listed as a "periodic table" in Table V, have filled outer s-orbitals. These electrons do not participate in chemical bonding, but they are space-filling and make the ions decidedly non-spherical. The large and extended lone pair orbitals make these ions highly polarizable. This property is the reason that so many lead and bismuth compounds are interesting dielectric materials.

Table IV. Some important ternary structure types

Structure	Prototype	Coor. No. A	Coor. No. B	Space Group
ABX_2				
Chalcopyrite	$CuFeS_2$	4	4	$I\bar{4}2d$
β-$NaFeO_2$	β-$NaFeO_2$	4	4	$Pna2_1$
α-$NaFeO_2$	α-$NaFeO_2$	6	6	$R\bar{3}m$
α-$LiFeO_2$	α-$LiFeO_2$	6	6	$I4_1/amd$
Delafossite	$CuFeO_2$	2	6	$R\bar{3}m$
ABX_3				
Calcite	$CaCO_3$	6	3	$R\bar{3}c$
Aragonite	$CaCO_3$	9	3	Pbnm
Ilmenite	$FeTiO_3$	6	6	$R\bar{3}$
Perovskite	$SrTiO_3$	12	6	Pm3m
ABX_4				
Silica Isotypes	$AlPO_4$	4	4	$P3_121$
Wolframite	$FeWO_4$	6	6	P2/c
Zircon	$ZrSiO_4$	8	4	$I4_1/amd$
Scheelite	$CaWO_4$	8	4	$I4_1/a$
Monazite	$CePO_4$	8	4	$P2_1/n$
Fergusonite	$YTaO_4$	8	4	I2
Anhydrite	$CaSO_4$	8	4	Cmcm
Barite	$BaSO_4$	12	4	Pnma
A_2BX_4				
Phenakite	Be_2SiO_4	4	4	$R\bar{3}$
Olivine	Mg_2SiO_4	6	4	Pbnm
Spinel	Al_2MgO_4	6	4	Fd3m
Thenardite	Na_2SO_4-V	6	4	Fddd
Sr_2PbO_4	Sr_2PbO_4	7	6	Pbam
K_2NiF_4	K_2NiF_4	9	6	I4/mmm
$CaFe_2O_4$	$CaFe_2O_4$	8	6	Pnam
$BaAl_2O_4$	$BaAl_2O_4$	9	4	$P6_322$
Th_3P_4	$CaLa_2S_4$	8	8	$I\bar{4}3d$

Table V. A "periodic table" of non-bonding, lone pair ions

		As^{3+}
	Sn^{2+}	Sb^{3+}
Tl^{+}	Pb^{2+}	Bi^{3+}

The Primary Structure: Perovskite

The ideal perovskite structure consists of a three dimensional network of corner-sharing octahedra with a large ion in the 12-coordinated site created by the space between the octahedra (Fig. 5).

THREE VIEWS OF PEROVSKITE

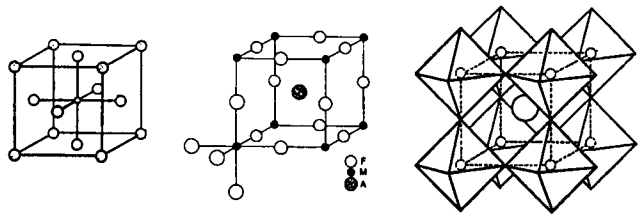

Figure 5: Three views of the perovskite structure, AMX_3. Left) Unit cell with 6-coordination M-ion at center. Middle) Unit cell with 12-coordination A ion at center. Right) Unit cell displaying framework of corner-sharing octahedral.

The ideal structure is cubic, space group Pm3m, with a single ABX_3 formula in the primitive unit cell. The mineral perovskite, $CaTiO_3$, is an orthorhombic distortion of the ideal structure so $SrTiO_3$ is often taken as the prototype. The ideal cubic perovskite structure is relatively unstable against distortions of various kinds but the overall structural arrangement is extremely stable and permits a great variety of ionic substitutions. Goldschmidt pointed out long ago that the stability range of the perovskite structure could be described by a tolerance factor defined as

$$t = \frac{(R_A + R_X)}{\sqrt{2}(R_B + R_X)}$$

The tolerance factor ranges from 0.8 to 0.9 for perovskite structures and from 0.7 to 1.0 if various distorted derivatives are included.

The examples given below all have the basic perovskite arrangement but not all have the ideal cubic perovskite structure. The term "perovskite" structure is applied to the entire set of related structures whereas the Pm3m cubic structure is called the "ideal perovskite structure".