

Crystal Structure–Physical Property Relationships in Perovskites

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Abstract

The crystal structures of seven compounds with the perovskite structure are analysed in terms of their cation coordination polyhedra. The analysis shows that the occurrence of ferroelectricity in a perovskite of composition ABO_3 requires the ratio of cuboctahedral A -ion volume to octahedral B -ion volume to be exactly five, and that there is a minimum octahedral B -ion volume associated with ferroelectric properties. The analysis also suggests that each ion may be assigned a characteristic range of polyhedral volumes which is transferable to other crystal structures. The methodology is applied to two perovskite ceramic systems, lead zirconate titanate (PZT) and lead zinc niobate (PZN). The phase diagram of the PZT system is rationalized in terms of the coordination polyhedra of the lead, zirconium and titanium ions, and a critical lead cuboctahedral volume is defined at the morphotropic phase boundary. The effect of the lanthanum ion in stabilizing the tetragonal phase to a higher Zr/Ti ratio and in reducing the Curie temperature is also discussed. In the PZN system the polyhedral analysis permits a rationalization of the behaviour of seven different additives in inhibiting the formation of a pyrochlore phase, $Pb_3Nb_4O_{13}$, during the fabrication of PZN ceramic. The potential of the technique as a predictive structural tool is also assessed.

Introduction

The investigation of *quantitative* relationships between crystal structure and physical properties falls naturally within the boundaries of Materials Science. Most of the advances in the knowledge of properties of materials have been the outcome of a systematic observation of the properties of closely related materials, since it is often small crystal or microstructural differences which are associated with marked changes in physical properties. The formulation of crystal structure–physical property relationships in materials requires a means of *measuring* crystal structures in an appropriate, quantitative manner for the physical property under investigation. The crystal structure of any metal oxide is defined unambiguously by its unit-cell constants, the space group, and the identities and positional coordinates of its constituent ions. If a comparison of

several structures is sought, however, the amount of data contained in such a description is too large to be meaningful, and a more general description is desirable. In view of the translational symmetry inherent in any regular crystal structure, it is often helpful to define structural units or ‘building blocks’ from which the entire crystal can be constructed. Traditionally these have been taken either as the crystallographic unit cells, or alternatively, the individual ions have been regarded as the basic structural units. Characteristic ionic radii have been tabulated for all elements in the periodic table in a variety of oxidation states, electron-spin states and coordination numbers (Shannon, 1976), and gross structural trends can be rationalized in these terms. A third option, however, is to consider the metal cations and their associated oxygen-ion coordination polyhedra as the building blocks.

Hazen (1977) has proposed that the cation coordination polyhedron can be regarded as the fundamental unit of ‘structure’ in a study of the variation of crystal structure with temperature, pressure and composition. Three different properties of a cation coordination polyhedron have been selected: volume, quadratic elongation and bond-angle variance (Robinson, Gibbs & Ribbe, 1971). The latter two quantities are defined as follows:

$$\text{quadratic elongation } \lambda = \sum_{i=1}^n (l_i/l_0)^2/n, \quad (1)$$

$$\text{bond-angle variance } \sigma = \sum_{i=1}^n (\theta_i - \theta_0)^2/(n-1), \quad (2)$$

where l_0 and θ_0 are bond lengths and angles in regular polyhedra. For tetrahedral coordination, $n = 4$ and $\theta_0 = 109.47^\circ$, whereas for octahedral coordination, $n = 6$ and $\theta_0 = 90^\circ$. The procedure for calculating the volumes of tetrahedra and octahedra has been described by Swanson & Peterson (1980). Since all the exterior faces are triangular, the volume is calculated by summing the volumes of elementary tetrahedra based on each of the faces, with a common apex inside the polyhedron.

The potential advantages of this approach are threefold:

(i) It can be applied to structures with an asymmetrical coordination of cations, which cannot be

represented accurately by the close-packing of spherical ions.

(ii) The observed variation in polyhedral volume, quadratic elongation and angle variance reflects the subtle chemical differences both between different cations and also between cations of the same kind in different crystal structures.

(iii) A large number of crystal structures can be regarded as composed of adjoining coordination polyhedra, such that there is no 'free', 'empty' or interstitial volume. This contrasts with the spherical-ion model in which free volume is unavoidable. The absence of free volume permits a quantification of the relationship between polyhedral volumes and the volume of the unit cell, a quantity which is readily determined from X-ray diffraction experiments.

In order to assess the potential of this methodology, the conditions for the stability of the perovskite structure will be examined in terms of cation coordination polyhedra. Perovskites have attracted much scientific and technological interest over the past forty years. This interest can be attributed, in part, to the discovery of ferroelectricity in barium titanate, BaTiO_3 , and the subsequent exploration of related ferroelectric perovskites such as lead titanate, PbTiO_3 , and the complex perovskite, lead magnesium niobate, $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$. Materials of this kind have found wide application in electronic devices such as ceramic multilayer capacitors, piezoelectric transducers, pyroelectric detectors and gas sensors. The relative ease with which these materials can be manufactured in ceramic form facilitates bulk manufacture of these devices, and there exists a wide body of knowledge concerning the compositions and microstructures of perovskite ceramics, required for the optimization of various properties. It can be argued, therefore, that the technological manipulation of perovskite ceramics has preceded a full scientific understanding of their behaviour. The tailoring of perovskites to produce materials with a given set of properties involves careful

control of composition and impurity levels, and the final chemical composition is usually determined by the lengthy process of trial and error. In this context, the idea of a cation coordination polyhedron will be used to define an analytical framework in which experimentally observed structural variations can be correlated with changes in the dielectric properties of these materials. Any correlations found can subsequently be used to suggest changes in chemical composition which are likely to result in improved or amended physical properties of the materials.

Method

The starting point for the polyhedral analysis is the crystal structure data of perovskite systems, which are available in the literature. These data are obtained either from X-ray single-crystal or polycrystalline neutron diffraction studies, and they provide details of unit-cell constants, space symmetry and atomic coordinates. The positions of the oxygen ions coordinating each symmetry-independent cation are evaluated, and the three polyhedral properties, quadratic elongation, bond-angle variance and polyhedral volume, are calculated from this information. A FORTRAN77 program has been written to perform these calculations (Thomas, 1988).

Since any structure of the perovskite type can be regarded as a juxtaposition of AO_{12} cuboctahedra and BO_6 octahedra (see Fig. 1), a means of calculating the volume of a cuboctahedron must be defined. A regular cuboctahedron consists of eight triangular and six square faces and the contribution of the triangular faces to the polyhedral volume can be calculated according to the method of Swanson & Peterson (1980). The square faces must be divided into two triangular sub-faces before the method is applied, and Thomas (1988) has developed an algorithm to perform this task. In the case of the regular cuboctahedron the extension is trivial, but there exist distorted forms of the polyhedron in which

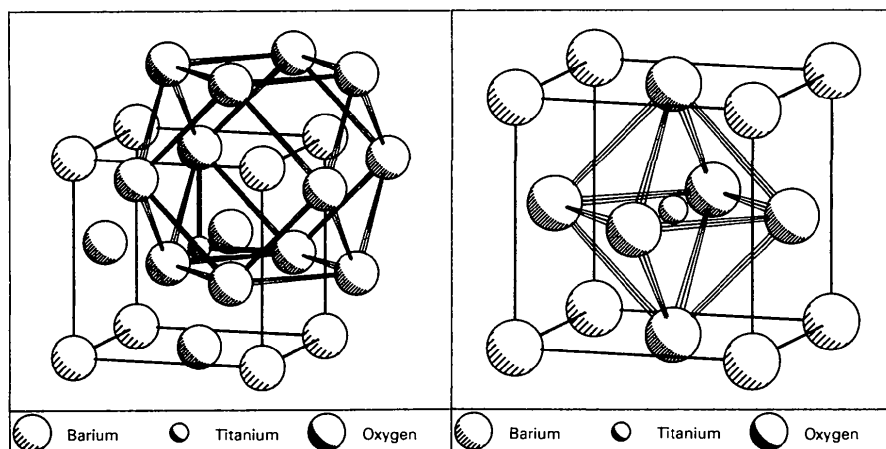


Fig. 1. A representation of barium titanate, BaTiO_3 , (cubic $m3m$ structure) as a juxtaposition of AO_{12} cuboctahedra and BO_6 octahedra.

Table 1. *A polyhedral analysis of perovskite structures, ABO₃*

Compound (ABO ₃)	Temp. (K)	Symmetry	Dielectric property									Ref.	
				Z	V _A (Å ³)	V _B (Å ³)	V _A /V _B	λ _A	λ _B	σ _A	σ _B		
BaTiO ₃	474	c <i>m3m</i>	p	1	53.8067	10.7614	5.000	1.0000	1.0000	0.000	0.000	(1)	
	r.t.	t <i>4mm</i>	f	1	53.6322	10.7264	5.000	1.0007	1.0041	1.250	7.905	(2)	
	?	o <i>mm</i>	f	2	53.5512	10.7102	5.000	1.0006	1.0040	1.069	7.697	(1)	
PbTiO ₃	77	r <i>3m</i>	f	1	53.3728	10.6746	5.000	1.0011	1.0085	1.989	16.574	(3)	
	823	c <i>m3m</i>	p	1	52.1423	10.4285	5.000	1.0000	1.0000	0.000	0.000	(4)	
	298	t <i>4mm</i>	f	1	52.8125	10.5625	5.000	1.0309	1.0275	33.764	65.419		
	158	t <i>4mm</i>	f	1	52.7896	10.5579	5.000	1.0329	1.0286	33.254	69.288		
SrTiO ₃	90	t <i>4mm</i>	f	1	52.7320	10.5464	5.000	1.0337	1.0302	36.691	71.532		
	r.t.	c <i>m3m</i>	p	1	49.5848	9.9170	5.000	1.0000	1.0000	0.000	0.000	(5)	
CaTiO ₃	r.t.	o <i>mmm</i>	nd	4	46.3007	9.4958	4.876	1.0058	1.0012	10.458	4.127	(6)	
KNbO ₃	698	c <i>m3m</i>	p	1	54.1939	10.8388	5.000	1.0000	1.0000	0.000	0.000	(7)	
	543	t <i>4mm</i>	f	1	54.0921	10.8184	5.000	1.0014	1.0068	1.486	16.448	(8)	
	r.t.	o <i>mm</i>	f	2	53.9271	10.7854	5.000	0.9984	1.0080	2.350	13.636	(9)	
NaNbO ₃	236	r <i>3m</i>	f	1	53.9751	10.7950	5.000	1.0020	1.0118	2.614	26.021	(10)	
	923	c <i>m3m</i>	p	1	50.7483	10.1497	5.000	1.0000	1.0000	0.000	0.000	(11)	
	873	t <i>4/mmm</i>	p	2	50.8206	10.2081	4.978	0.9937	1.0000	0.693	0.000	(11)	
	IV	r.t.	o <i>mmm</i>	af	8	49.1123	10.3637	4.739	1.0210	1.0058	8.700	14.868	(12)
NaTaO ₃	IV	r.t.	o <i>mmm</i>	af	4	48.5831	10.1078	4.806	1.0040	1.0002	9.020	0.530	(13)

Notes: af = antiferroelectric, c = cubic, f = ferroelectric, nd = normal dielectric, o = orthorhombic, p = paraelectric, r = rhombohedral, t = tetragonal.

References: (1) Wyckoff (1964); (2) Harada, Pedersen & Barnea (1970); (3) Hewat (1974); (4) Glazer & Mabud (1978); (5) Roth (1957); (6) Kay & Bailey (1957); (7) Shirane, Newnham & Pepinsky (1954); (8) Hewat (1973a); (9) Katz & Megaw (1967); (10) Hewat (1973b); (11) Glazer & Megaw (1972); (12) Sakowski-Cowley, Lukaszewicz & Megaw (1969); (13) Ahtee & Unonius (1977).

* Two symmetry-independent sodium ions in the unit cell.

the four oxygen atoms of a four-sided face are no longer strictly planar. Such 'non-planar faces' may still be divided into two triangles, but the division can be carried out in two different ways. Owing to the non-planarity of the four vertices, the contribution of a given four-sided 'face' to the cuboctahedral volume is dependent on the way in which the triangular splitting is performed. Care is taken that the splitting gives rise to cuboctahedra with split four-sided faces which interlock perfectly with adjacent polyhedra. Only in this way are the calculated cuboctahedral volumes correct, and in the case of perovskites, an independent check can be carried out according to:

$$V_u = \mathbf{a} \cdot \mathbf{b} \wedge \mathbf{c} = \sum_{i=1}^Z (V_{i,\text{oct}} + V_{i,\text{cuboct}}). \quad (3)$$

In this expression, V_u is the volume of the unit cell, which can be calculated either from the triple scalar product of the unit-cell vectors \mathbf{a} , \mathbf{b} and \mathbf{c} , or from a summation of the cuboctahedral and octahedral volumes $V_{i,\text{cuboct}}$ and $V_{i,\text{oct}}$ of the A and B ions respectively. Z is the number of ABO_3 formula units in the unit cell.

Calculation of the quadratic elongation and bond-angle variance of the BO_6 octahedra in perovskites is performed according to (1) and (2) respectively. For the AO_{12} cuboctahedra, (1) and (2) are also used, with n equal to 12 and θ_0 equal to 60° .

Application of the polyhedral analysis to known perovskite structures

The analysis is first applied to some perovskite systems which are of interest because of their dielectric properties. Since the method of analysis has no inbuilt

assumptions concerning structure, it must first be applied to known perovskite crystal structures. Once any trends and discriminating properties have been detected the method can be used to predict the structures and associated properties of further compositions for which full crystal structural data are not available.

A polyhedral analysis has been made of seven perovskite compounds with fully documented crystal structures. The results are summarised in Table 1, and the following trends are observed:

V_A . In the ferroelectric compounds BaTiO₃ and KNbO₃, V_A is greatest in the cubic, paraelectric phases. This is not the case in ferroelectric PbTiO₃, where V_A is minimum in the cubic phase. The difference in behaviour can be attributed to a change in the *effective* coordination number of the lead ion from 8 to 12 in passing from the ferroelectric to the paraelectric state. Ranges of observed cuboctahedral volumes can be established for 12-fold coordination of Ba²⁺, Pb²⁺, Sr²⁺, Ca²⁺, K⁺ and Na⁺ ions, for a range of temperature defined in Table 1. For Ba²⁺, $53.373 < V_A < 53.807 \text{ \AA}^3$; Pb²⁺, $52.142 < V_A < 52.813 \text{ \AA}^3$; Sr²⁺, $V_A \approx 49.585 \text{ \AA}^3$; Ca²⁺, $V_A \approx 46.301 \text{ \AA}^3$; K⁺, $53.927 < V_A < 54.194 \text{ \AA}^3$; Na⁺, $48.583 < V_A < 50.821 \text{ \AA}^3$.

V_B . In all of the cubic *m3m*, tetragonal *4mm*, orthorhombic *mm* and rhombohedral *3m* structures, V_B is exactly one fifth of V_A , giving rise to trends in V_B which are parallel to those in V_A . In the case of the centrosymmetric orthorhombic *mmm* and tetragonal *4/mmm* structures, the V_A/V_B ratio is less than five. Ranges of observed octahedral volumes can be established for sixfold coordination of Ti, Nb and Ta ions: Ti⁴⁺, $9.496 < V_B < 10.761 \text{ \AA}^3$; Nb⁵⁺, $10.150 < V_B < 10.839 \text{ \AA}^3$; Ta⁵⁺, $V_B \approx 10.108 \text{ \AA}^3$.

λ_A, λ_B . These quadratic elongation parameters are equal to one for all cubic $m3m$ structures. The deviations from unity are greatest in PbTiO_3 , where the Pb and Ti ions are displaced significantly from the centres of their respective oxygen cuboctahedra and octahedra.

σ_A, σ_B . These bond-angle variances are well correlated with the values for quadratic elongation. σ_A and σ_B bear an approximately linear relationship to λ_A and λ_B , as proposed by Robinson *et al.* (1971). The extent of the linearity has been quantified by performing a least-squares fitting of a straight line to the values of (λ_A, σ_A) and (λ_B, σ_B) quoted in Table 1. $|\lambda_A - 1| = 8.919 \times 10^{-4} \sigma_A$, residual 3.766×10^{-3} ; $|\lambda_B - 1| = 4.176 \times 10^{-4} \sigma_B$, residual 7.040×10^{-4} .

The exact V_A/V_B ratio of five in the non-centrosymmetric perovskite structures is a fixed geometrical constraint for ferroelectric behaviour to occur in perovskites. Values of this ratio less than five are associated with centrosymmetric structures which are incapable of exhibiting ferroelectricity. Although strontium titanate has a V_A/V_B ratio ideally suited for ferroelectricity, the volume of the titanium octahedron is sufficiently small for the metal ion to be stabilized at the centre of the octahedron. As the volume of the TiO_6 octahedron increases (as in PbTiO_3 and BaTiO_3), the titanium ion can be stabilized at an off-centre position within the oxygen octahedron, giving rise to a spontaneous polarization (Thomas, 1989). It would seem reasonable, therefore, to postulate a *minimum* TiO_6 octahedral volume for ferroelectricity to occur, which lies in the range $9.917 < V_B < 10.428 \text{ \AA}^3$.

It is instructive to define the relationship between a geometrical analysis based upon polyhedral volumes and the popular, alternative analysis based upon idealized ionic radii. A perfectly spherical cation in contact with all its coordinating oxygen ions would give rise to a regular coordination polyhedron with a volume expressed in terms of the relevant centre-to-vertex distance, $(R_A + R_0)$ or $(R_B + R_0)$. For a regular cuboctahedron, $V_A = 10/(3 \times 2^{1/2})(R_A + R_0)^3$ and for a regular octahedron, $V_B = \frac{4}{3}(R_B + R_0)^3$. Thus the ratio V_A/V_B in the idealized case is equal to $5/(2 \times 2^{1/2})(R_A + R_0/R_B + R_0)^3$, and the observed value of five for V_A/V_B in cubic $m3m$ perovskites requires that

$$R_A + R_0 = 2^{1/2}(R_B + R_0). \quad (4)$$

This is the equality which has commonly been used as a stability criterion for perovskites. The Goldschmidt tolerance factor, t , is given by $(R_A + R_0)/2^{1/2}(R_B + R_0)$, and this has the value one when $V_A/V_B = 5$. It is generally assumed that the perovskite phase is stabilized if t has a value close to one. Thus the Goldschmidt analysis assumes fixed idealized ionic radii, with a tolerance allowed in the geometric criterion. Conversely, the polyhedral coordination approach assumes a fixed geometrical criterion for the stabilization of the

ferroelectric perovskite phase, with a tolerance allowed in the characteristic polyhedral volumes of each cation. The advantage of the latter approach is that the values of V_A and V_B are experimentally determined for each crystal structure, and no reference is made to *average* ionic radii or polyhedral volumes. It is undesirable to reduce these derived ranges of polyhedral volumes to a representative average value since much valuable structural information is accommodated by considering allowed *ranges* of ionic sizes. It should be possible to establish characteristic ranges of polyhedral volumes for each ion, which are transferable between different structures. For example, in the compounds listed in Table 1 the six-coordinated titanium ion is found with a wide range of polyhedral volumes between 9.496 and 10.761 \AA^3 , whereas the 12-coordinated barium ion is found within a narrower range of polyhedral volumes between 53.373 and 53.807 \AA^3 .

Application of the polyhedral analysis to perovskite ceramics

The majority of perovskite ceramics of technological importance are multiphase and/or multicomponent systems in which the short-range order cannot be probed by conventional X-ray or neutron diffraction techniques. Since neutron powder diffraction studies can reveal only an averaged unit cell, additional information such as that provided by characteristic ranges of polyhedral volumes, is helpful in relating gross structural information to dielectric properties. Two ceramic systems have been selected for a polyhedral analysis. The first of these is the lead zirconate-lead titanate (PbZrO_3 - PbTiO_3) system, which includes compositions with extremely strong piezoelectric effects (Jaffe, Cook & Jaffe, 1971). The

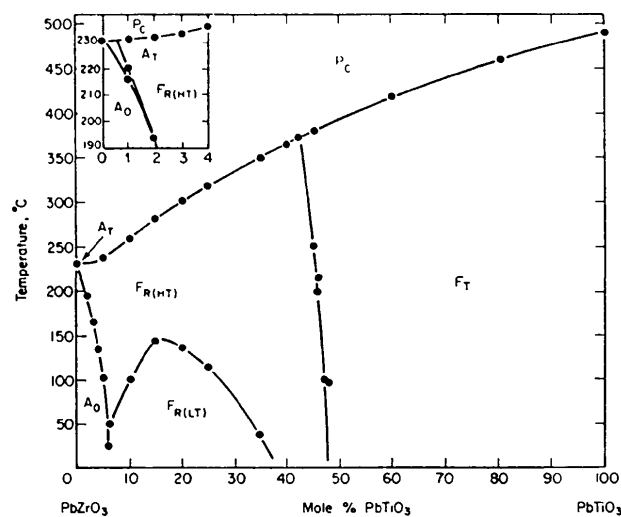


Fig. 2. The temperature-composition phase diagram of the PZT system, $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$, (after Jaffe, Cook & Jaffe, 1971).

Table 2. *A polyhedral analysis of lead zirconate and lead zirconate titanate*

System	Phase	V_{pb}	$V_{Zr/Ti}$	V_A/V_B	λ_A	λ_B	Temp. (K)
PbZrO ₃ *	A_o	59.071	11.934	4.950	1.0322	1.0305	r.t.
		59.356†		4.974†	1.0289†		
PZT‡	F_R (LT)	59.042	11.935	4.947	1.0288	1.0071	298
PZT	F_R (LT)	59.131	11.927	4.958	1.0265	1.0066	333
PZT	F_R (HT)	59.332	11.866	5.0003	1.0174	1.0048	373
PZT	F_R (HT)	59.388	11.877	5.0003	1.0160	1.0030	423
PZT	F_R (HT)	59.411	11.881	5.0003	1.0081	1.0026	473
PZT	F_R (HT)	59.386	11.876	5.0003	1.0052	1.0003	508
PZT	P_c	59.342	11.868	5.0000	1.0000	1.0000	573

* Reference: Wyckoff (1964).

† Two symmetry-independent lead ions in the unit cell.

‡ Reference: Glazer, Mabud & Clarke (1978).

second system is lead zinc niobate, which is relevant to the fabrication of multilayer ceramic capacitors at lower firing temperatures (Suvorov, Devoino, Kolar & Trontelj, 1988).

Phase relationships in the PZT system

The lead zirconate titanate (PZT) system, PbZrO₃–PbTiO₃, has a phase diagram as shown in Fig. 2. P_c represents the paraelectric cubic phase, A_o an antiferroelectric orthorhombic phase, F_T a ferroelectric tetragonal phase, and F_R (LT) and F_R (HT) the low- and high-temperature forms of a rhombohedral ferroelectric phase. The results of a polyhedral analysis of the pure PbZrO₃ A_o phase and the Pb(Zr_{0.9}Ti_{0.1})O₃ composition are given in Table 2. The PbZrO₃ structure has been evaluated at room temperature whereas data for the PZT composition have been collected at a range of temperatures between 298 and 573 K, which encompasses the F_R (LT), F_R (HT) and P_c phases (Glazer, Mabud & Clarke, 1978).

Several trends can be discerned from Table 2:

(i) The volume of the 12-coordinated Pb²⁺ ion lies in the range between 59.042 and 59.411 Å³.

(ii) The volume of the six-coordinated Zr⁴⁺ ion is 11.934 Å³ in PbZrO₃.

(iii) The volume of six-coordinated (Zr_{0.9}/Ti_{0.1}) varies between 11.866 and 11.935 Å³ in the PZT composition.

(iv) Values of λ_A and λ_B in PZT, representing quadratic elongation, decrease systematically as the temperature is increased towards the Curie temperature. In PbZrO₃, both λ_A and λ_B are large, indicating that both Pb²⁺ and Zr⁴⁺ have a highly asymmetric oxygen coordination in which the cations are displaced significantly from the centres of their coordination polyhedra.

(v) Characteristic V_A/V_B ratios can be assigned to each structural type: in PbZrO₃ (A_o), $\langle V_A/V_B \rangle = 4.962$; in PZT [F_R (LT)], $\langle V_A/V_B \rangle = 4.953$; in PZT [F_R (HT)], $\langle V_A/V_B \rangle = 5.0003$; in PZT (F_T and P_c), $V_A/V_B = 5$. The variation in V_A/V_B ratios is small, indicating the gross structural similarity of all the phases under consideration. The small reduction in

V_A/V_B at the high Zr⁴⁺ end of the composition range, however, suggests that there is a maximum allowed size of the lead coordination polyhedron. When Zr⁴⁺ is the B ion, this maximum would be exceeded by a V_A/V_B ratio of five.

Of particular interest in the PZT system is the occurrence of a morphotropic phase boundary (MPB) at the composition of approximately 47 mol% titanium. The composition at which this boundary occurs is almost independent of temperature, and it is marked by a change from tetragonal distortion of the coordination polyhedra in the F_T phase to a trigonal distortion in the F_R (HT) phase. The piezoelectric electromechanical coupling factors and the relative permittivity are highest near the MPB, and stability of electromechanical properties over a wide range of temperature is ensured. There is no significant difference in V_A/V_B ratio between the F_T and F_R (HT) phases, but the reduction to threefold symmetry permits tilting of the Zr–O octahedra and coordination of the lead ion. This tilting is essential as the volume of the Zr⁴⁺ octahedra is increased in compositions richer in zirconium, and the degree of tilting is reflected in the values of λ_A and λ_B , which increase markedly in the F_R (LT) phase.

If a linear variation of V_A is assumed for PZT compositions between pure lead titanate (PT) and Pb(Zr_{0.9}Ti_{0.1})O₃, it is possible to propose a critical polyhedral volume for the lead ion, which is associated with the MPB. For PT, $V_A = 52.812 \text{ \AA}^3$, and for the PZT composition, $V_A = 59.042 \text{ \AA}^3$ at room temperature. Thus for a general composition Pb(Zr_{1-x}Ti_x)O₃,

$$V_A = V_{pb} = 59.042 - \frac{(10x - 1)}{9} (59.042 - 52.812) \quad (x > 0.1). \quad (5)$$

Substitution with $x = 0.47$ gives rise to a critical value of $V_{pb} = 56.481 \text{ \AA}^3$ at the MPB. An independent assessment of the validity of (5) is given by calculating V_{pb} for the $x = 0.35$ composition. The calculation gives $V_{pb} = 57.311 \text{ \AA}^3$, with a corresponding unit-cell volume, $\frac{5}{3}V_{pb}$, equal to 68.77 \AA^3 . This result compares favourably with the value of 68.60 \AA^3 obtained for Pb(Zr_{0.65}Ti_{0.35})O₃ by Haertling & Land (1971). These workers have also shown that the addition of La³⁺ to PZT causes a progressive shift in the MPB, such that the F_T phase is stabilized at richer zirconium compositions than in undoped PZT. In undoped PZT, the MPB occurs at a composition of approximately 53 mol% Zr⁴⁺, whereas in PZT doped with 9 mol% La³⁺, the MPB is shifted to approximately 65 mol% Zr⁴⁺. The addition of lanthanum appears not to affect the unit-cell volume of Pb(Zr_{0.65}Ti_{0.35})O₃ significantly, but the ionic radii of Shannon (1976) suggest that La³⁺ should have a smaller cuboctahedral volume than Pb²⁺. The addition of lanthanum also introduces cation vacancies in the crystal structure, since the valence of lanthanum is

Table 3. *Compounds added to PZN to stabilize the perovskite phase [data from Halliyal et al. (1987); see text re right-hand column]*

Additive	Amount (mol %)	Tolerance factor t	Electronegativity difference	Active stabilizing ion(s)
BaTiO ₃	6-7	1.06	2.30	Ba ²⁺ , Ti ⁴⁺
SrTiO ₃	9-10	0.99	2.25	Ti ⁴⁺
PbTiO ₃	25-30	1.02	1.84	Ti ⁴⁺
BaZrO ₃	15-18	1.00	2.36	Ba ²⁺
Ba(Zn _{1/3} Nb _{2/3})O ₃	15	1.02	2.25	Ba ²⁺
Replacing Pb with K	10	—	—	K ⁺
PbZrO ₃	55-60	0.96	1.90	None

higher than that of lead. There is some debate as to whether these vacancies occur predominantly at the *A*- or the *B*-ion sites, but either mechanism can account for the stabilization of the F_T phase at higher zirconium compositions.

Stabilization of the F_T phase depends upon tetragonal distortion and coupling of the lead cuboctahedra, which break down at the MPB when the volume of the *B* ions becomes too large. *A*-ion vacancies would enable the *B*-ion octahedra to expand further before the F_T phase disrupts whereas *B*-ion vacancies would reduce the average size of the *B*-ion octahedra. Both mechanisms would facilitate larger Zr/Ti ratios in the F_T phase. Another marked effect of lanthanum substitution is to reduce the Curie temperature across the Zr/Ti composition range. This can be interpreted as a progressive breaking up of the coupling between lead cuboctahedra, which is responsible for stabilizing the tetragonal and rhombohedral phases below the Curie temperature.

Stabilization of PZN ceramic in the perovskite phase

Lead zinc niobate (PZN), Pb(Zn_{1/3}Nb_{2/3})O, is a relaxor ferroelectric which exhibits a diffuse ferroelectric-paraelectric phase transition with a maximum in the relative permittivity at approximately 413 K. The use of conventional solid-state reactions to prepare pure PZN with the perovskite structure has generally been unsuccessful, as a stable pyrochlore phase of type Pb₃Nb₄O₁₃ is formed preferentially. The presence of this phase downgrades the dielectric properties of the PZN phase. Halliyal, Kumar, Newnham & Cross (1987) have reported the compounds which can be added to the reaction mixture to stabilize PZN in the perovskite phase, and their findings are summarized in Table 3. These authors argue that a stable perovskite is formed only when the ionic radii of the cations fall within the limits defined by the Goldschmidt criterion, *and* when the cation-anion bonding is strongly ionic. Barium titanate, it is argued, is particularly stable in the perovskite structure because of its large tolerance factor, t , [(see (4))] and also because of its large mean electronegativity difference $[(\chi_{A-O} + \chi_{B-O})/2]$. A rationalization is thus given for the effectiveness of

barium titanate in stabilizing PZN in the perovskite structure. Two questions are immediately raised by the arguments of Halliyal et al. (1987). First, why should a tolerance factor of 1.06 be associated with a more stable perovskite structure than a perovskite phase of tolerance factor 1.00? Secondly, although the bonding in perovskites is predominantly ionic, why should a high ionicity be a *requirement* for stabilizing the perovskite structure?

A consideration of characteristic polyhedral volumes for the lead, zinc and niobium ions suggests why stabilizing the perovskite phase in PZN is difficult. In order to discuss the stabilizing effects of the different compounds in full, typical values of octahedral volumes have been evaluated in Table 4, for six-coordinated Zn²⁺, Zr⁴⁺, Mg²⁺ and W⁶⁺ ions in a variety of crystal structures at room temperature. The following ranges of octahedral volume can be inferred: $11.597 < V_{Zn^{2+}} < 12.087$; $11.597 < V_{Zr^{4+}} < 12.285$; $11.405 < V_{Mg^{2+}} < 11.989$; $9.072 < V_{W^{6+}} < 9.533 \text{ \AA}^3$. In addition, the upper limit of the cuboctahedral volume range for the Ba²⁺ ion can be extended on account of the known cubic perovskite structure of BaZrO₃, which has a unit-cell constant of 4.1929 Å at room temperature (Wyckoff, 1964). The proposed volume range for barium at room temperature is therefore: $53.632 < V_{Ba^{2+}} < 61.427 \text{ \AA}^3$. The above analysis of PZT suggests a volume range for the lead ion of $52.812 < V_{Pb^{2+}} < 59.356 \text{ \AA}^3$ at room temperature. These polyhedral volume ranges are displayed graphically in Fig. 3, together with the volume ranges of the Ti⁴⁺ and Nb⁵⁺ ions at room temperature, established from Table 1. In order to facilitate comparison, the *B*-ion volumes are represented as their *A*-ion equivalents, by multiplying their volumes by five. This can be done because of the fixed V_A/V_B ratio of five in the perovskite structure.

It is seen that the zinc ion can be stabilized in the perovskite phase only for larger values of $V_{Pb^{2+}}$, whereas stabilization of the niobium ion requires a smaller value of $V_{Pb^{2+}}$. It is expected, therefore, that there is some *local* variation in the polyhedral volumes of the lead ions, which is not detected by conventional diffraction experiments. This is likely to produce both lattice strain and a limited separation of niobium-rich and zinc-rich areas. Separation of this kind has been postulated as the structural basis for the 'relaxor' dielectric response (Thomas, 1989). Addition of the Ti⁴⁺ ion is likely to inhibit pyrochlore formation, since its volume range overlaps considerably with that of the niobium ion, and it will favour a *local* tetragonal distortion characteristic of the lead titanate structure. The Ba²⁺ ion does not inhibit the formation of pyrochlore directly, but rather stabilizes the perovskite phase in PZN by increasing the average volume of the *A* sites. With the addition of barium, the large Zn²⁺ ion can pack in the perovskite structure more easily, as the ideal V_A/V_B ratio of five can be attained.

Table 4. *Calculated polyhedral volumes (\AA^3) of six-coordinated Zn, Zr, Mg and W ions*

Ion	System	Volume	Ref.
Zn^{2+}	$\alpha\text{-Zn}_2\text{P}_2\text{O}_7$	12.087	(1)
	$\beta\text{-Zn}_2\text{P}_2\text{O}_7$	11.597	(2)
Zr^{4+}	BaZrO_3	12.285	(3)
	$\beta\text{-K}_2\text{Zr}_2\text{O}_7$	12.159	(4)
	Li_2ZrO_4	12.047	(5)
	$\text{NaZr}_2\text{P}_3\text{O}_{12}$	11.597	(6)
	$\text{Mg}_3\text{As}_2\text{O}_8^*$	11.989	(7)
Mg^{2+}	$\text{Mg}_2\text{P}_2\text{O}_7$	11.842	(8)
	$\text{Mg}_2\text{V}_2\text{O}_7$	11.741	(9)
	$\text{Mg}_3\text{As}_2\text{O}_8^*$	11.685	(7)
	MgSiO_3	11.678	(10)
	Mg_3TeO_6	11.405	(11)
	$\alpha\text{-SnWO}_4$	9.533	(12)
W^{6+}	$\text{NaIn}(\text{WO}_4)_2$	9.328	(13)
	CuWO_4	9.320	(14)
	Bi_2WO_6	9.072	(15)

References: (1) Robertson & Calvo (1970); (2) Calvo (1965*b*); (3) Wyckoff (1964); (4) Gatehouse & Lloyd (1970); (5) Ditttrich & Hoppe (1969); (6) Hagman & Kierkegaard (1968); (7) Krishnamachari & Calvo (1973); (8) Calvo (1965*a*); (9) Gopal & Calvo (1974); (10) Morimoto & Koto (1969); (11) Schulz & Bayer (1971); (12) Jeitschko & Sleight (1972); (13) Klevtsov & Klevtsova (1970); (14) Kihlborg & Gebert (1970); (15) Wolfe, Newnham & Kay (1969).

* Two symmetry-independent magnesium ions in the unit cell.

The stabilizing effect of barium titanate can thus be explained by the simultaneous action of both Ba^{2+} and Ti^{4+} ions. Most of the other additives in Table 3 utilize one or other of these two perovskite-stabilizing mechanisms. SrTiO_3 inhibits pyrochlore formation with its titanium ions, but does not stabilize zinc in the perovskite structure; the Sr^{2+} ion may even reduce the stabilization of the zinc ion in the perovskite phase. The poor stabilizing effect of PbTiO_3 is probably a result *not* of its titanium content, but rather of its stability as a phase with large tetragonal distortion; this is likely to reduce its miscibility with other phase(s). The zirconium ion is inactive in stabilizing PZN in the perovskite phase because its volume range is comparable to that of the zinc ion. Consequently, BaZrO_3 and

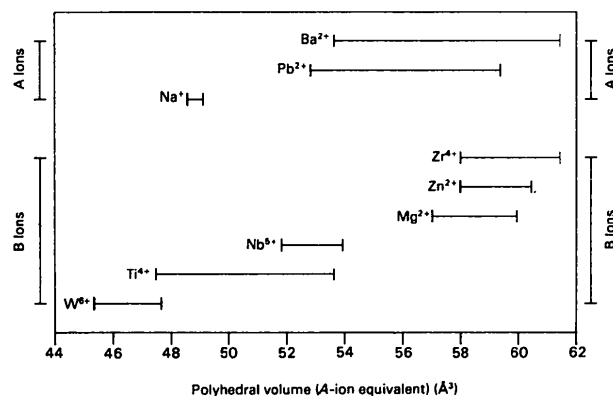


Fig. 3. A graphical representation of the room-temperature ranges of polyhedral volumes of the Ba^{2+} , Pb^{2+} and Na^+ A ions and the Zr^{4+} , Zn^{2+} , Mg^{2+} , Nb^{5+} , Ti^{4+} and W^{6+} B ions. The B -ion volumes are represented as their A -ion equivalents for stabilization in a ferroelectric perovskite structure.

$\text{Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ are stabilizers only because of their barium content. The comparable required amounts of these additives support this interpretation. K^+ acts similarly to the barium ion, in increasing the average volume of the A site, and PbZrO_3 is predicted to have no stabilizing effect whatsoever. This prediction is supported by the data in Table 3. At levels of addition of 60% PbZrO_3 , it is surely more correct to regard PZN as the additive to PbZrO_3 . A summary of the ions which are active in stabilizing the perovskite structure in PZN is given in the right-hand column of Table 3.

Use of the polyhedral analysis as a predictive tool

The polyhedral analysis described is best seen as a tool to be used by the experimentalist as a guide to future investigations. To illustrate how the method can be used the ceramic system $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$ (PMN-PMW) will be taken as an example. Fig. 3 shows the characteristic volume ranges of the lead, magnesium, niobium and tungsten ions, expressed as their A -ion equivalents. The tungsten ion is difficult to stabilize in a ferroelectric perovskite structure with lead, because its volume range does not overlap with that of the lead ion. The magnesium and niobium ions can be stabilized as a ferroelectric perovskite, but, as in PZN, some local variation of the lead-ion volume is anticipated. Prediction of the variation with composition of the unit-cell volume, V_u , for the PMN-PMW system would be straightforward only if the two components were ideally mixed. If ideal mixing is (incorrectly) assumed in this case, then a general composition, $(\text{PMN})_{1-x}(\text{PMW})_x$, would have a mean B -ion volume of

$$V_B = V_{\text{Mg}^{2+}} \frac{(x+2)}{6} + V_{\text{Nb}^{5+}} \frac{(2-2x)}{3} + V_{\text{W}^{6+}} \frac{x}{2}, \quad (6)$$

and a unit-cell volume equal to $6V_B$. The minimum octahedral volume for the magnesium ion should be assumed, together with the maximum octahedral volumes of the ranges of the niobium and tungsten ions. This is in order to bring all three types of ion into 'solid solution', with a minimum variation in lead-ion volume. Substitution of these volumes into (6) gives rise to the relationship: $V_u (\text{\AA}^3) = 65.950 - 3.136x$. This is in reasonable agreement with the variation observed by Nomura, Jang, Cross & Newnham (1979). It is also interesting to note that the pure PMW component adopts an orthorhombically distorted perovskite phase which is antiferroelectric. This is consistent with lead and tungsten ranges of polyhedral volumes which do not overlap for the stabilization of a ferroelectric perovskite phase.

Given that the tungsten ion is small in comparison to the titanium and niobium ions, it is possible that tungsten can form a ferroelectric perovskite in conjunc-

tion with the sodium ion. The relevant room-temperature volume ranges, expressed as A -ion equivalents are: $45.360 < V_{W^{6+}} < 47.665$ and $48.583 < V_{Na^+} < 49.112 \text{ \AA}^3$. It is to be expected, therefore, that the WO_6 octahedron will be sufficiently large for the tungsten ion to be stabilized at a polar, off-centre position. In order to bring the average B -ion valence down to five, the W^{6+} ion could be combined with the Ti^{4+} ion in a 1:1 ratio. The observed room-temperature volume range of the titanium ion (see Fig. 3) is consistent with stabilization in a perovskite structure, but the volume of the Ti^{4+} octahedron is likely to be too small for the titanium ions to be *ferroelectrically active*. Thus, the compound $Na(Ti_{1/2}W_{1/2})O_3$ is likely to have properties similar to $Pb(Sc_{1/2}Ta_{1/2})O_3$, in which the dielectric response varies between that of a normal and a relaxor ferroelectric (Thomas, 1989).

The polyhedral analysis offers a versatile framework for the observation and rationalization of structural trends. It can be applied to all crystallographic systems with electronic and mechanical properties dependent upon equilibria between structurally related phases.

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The Structure of K_2TeO_3 – an Experimental and Theoretical Study

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Abstract

The single-crystal structure of K_2TeO_3 is presented with $M_r = 253.8$, trigonal, $P\bar{3}$, $a = 6.279(2)$, $c =$

$7.069(4) \text{ \AA}$, $V = 241.4(2) \text{ \AA}^3$, $Z = 2$, $D_x = 3.492(3) \text{ Mg m}^{-3}$, $Mo K\alpha$, $\lambda = 0.71069 \text{ \AA}$, $\mu = 7.77 \text{ mm}^{-1}$, $F(000) = 228$, $T = 293 \text{ K}$, 572 observed reflections gave $R = 0.049$. The structure consists of

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