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Tolerance factor for pyrochlores and related structures

In this work a new empirical tolerance factor for compounds with pyrochlore structure is proposed. This suggested tolerance factor is based on experimental structural data and on the tolerance factors proposed. However, since it does not depend on the structural data, this new tolerance factor permits the prediction of some properties of these compounds directly. Also, a good structure stability field for the pyrochlore formation is observed when this tolerance factor is used.

1. Introduction

The tolerance factor t was proposed by Goldschmidt to describe the stability and distortion in perovskite structures (Goldschmidt, 1926). This geometrical parameter was defined for ABO_3 oxide perovskite compounds in terms of the ionic radii as

$$t = \frac{R_A + R_O}{2^{1/2}(R_B + R_O)}, \quad (1)$$

where R_A , R_B and R_O are the ionic radii of the A cation, B cation and oxygen, respectively. By definition, in perovskites, the tolerance factor provides a measure of how well the A -site cation fits the 12-fold coordinated space within the corner-shared octahedral network formed by the B -site cation. Thus, this parameter indicates how far from ideal packing the ionic sizes from A and B cations can change, with fixed size for the oxygen anion, and the structure still remains an ideal perovskite. The value $t = 1$ indicates the ideal, in which the ions considered as perfect spheres are connected in a perfect cubic lattice. Values different from the ideal indicate distortions in the structure in relation to the ideal perovskite that are usually assumed as:

(i) for $t > 1$ the A cations are too large to fit into their sites and in this case hexagonal perovskites occur more frequently;

(ii) for $2^{1/2}/2 < t < 0.9$ the A cations are too small to fit into their sites and several possible perovskite-related distorted structures are proposed such as orthorhombic, tetragonal, monoclinic and rhombohedral structures, usually originating from BX_6 octahedral tilting to accommodate the small A cation;

(iii) for values lower than $t = 2^{1/2}/2$, when A and B cations have the same size, close-packed structures are observed as corundum, ilmenite and $KNbO_3$ -type (Ishihara, 2009).

Although the tolerance factor is a simple geometrical parameter based on the assumption of rigid spheres, it is a powerful tool to predict distortions in perovskite compounds and help to propose models for their physical properties. Useful correlations have been found between t and device-oriented properties of the materials. For example, Zürrmühlen

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et al. (1995) suggested that the restoring force constant of the lowest polar mode is strongly dependent on the tolerance factor, as well as the binding energy and dielectric constant of perovskite oxides. The tolerance factor is correlated to the typical highest wavenumber phonon with symmetry A_{1g} active in Raman scattering (Petzelt *et al.*, 1992; Zurmühlen *et al.*, 1994, 1995). Consequently, as the intrinsic losses are due to phonons, they define the dielectric applicability in the microwave frequency region. Even in other perovskite-related structures, such as piroxene (Cheng *et al.*, 2013), and antiperovskites (Zhao & Daemen, 2012), the tolerance factor plays an important role.

The oxide pyrochlores whose stoichiometry is $A_2B_2O_6X$ (where the anion X can be O, F or OH) are ternary or quaternary structures that like the perovskites are multifunctional, serving as appropriate crystallographic hosts for a wide range of applications, due to the great variety of possible site substitutions on both A and B sites. These substitutions imply an assortment of different physical properties, the main being magnetic frustration (Gardner & Greedan, 2010), but several other important properties, such as catalytic (Playford *et al.*, 2011; Oh *et al.*, 2012; Vega *et al.*, 2012), topological Hall effect (Ueda *et al.*, 2012), metal-insulator transitions (Yamaura *et al.*, 2012; Fujimoto, 2002), giant magnetoresistance (Shimakawa *et al.*, 1996; Subramanian *et al.*, 1996), analogous Dirac string and magnetic monopoles (Morris *et al.*, 2009; Castelnovo *et al.*, 2008), magnon Hall effects (Onose *et al.*, 2010), metallic ‘ferroelectricity’ (Sergienko *et al.*, 2004), ionic conduction (Lian *et al.*, 2001), superconductivity (Hanawa *et al.*, 2001; Vyaselev *et al.*, 2002; Kasahara *et al.*, 2006), ferroelectricity (Dong *et al.*, 2009, 2010) and quantum paraelectric behavior (Kamba *et al.*, 2007), are also observed. Thus, defining a tolerance factor for compounds with a pyrochlore-based structure is very useful, because it permits us (as in the perovskite case) to predict properties before synthesizing these compounds. Accordingly, Isupov (1958) and Cai *et al.* (2011) proposed different tolerance factors to describe the pyrochlore crystal structure. Isupov’s tolerance factor was more elegant and resembled that used to describe perovskites, although it was not so good for describing the structure stability field for pyrochlores. This was emphasized by Cai *et al.* (2011), who proposed two other expressions. However, both expressions depend either on the cubic lattice parameter or on independent oxygen-position parameters, which makes both difficult to calculate. In this work we derive an empirical tolerance factor for compounds with pyrochlore structure based only on the ionic radii of the constituent ions and investigate its correlation to structural, dielectric and phonon properties.

2. Previous tolerance factors for pyrochlores

The first tolerance factor proposed for oxide pyrochlores was defined by Isupov (1958) as

$$t = 0.866 \frac{R_A + R_O}{R_B + R_O}. \quad (2)$$

To derive it Isupov considered the BO_6 octahedra as perfect. Observe that this tolerance factor is similar to that proposed by Goldschmidt to describe the stability and distortion in perovskite structures (Goldschmidt, 1926). However, in the ideal pyrochlore structure $A_2B_2O_6X$, whose symmetry belongs to the space group $Fd\bar{3}m$, considering the B cation at the origin (origin 2), the A cations and the anion X are in special positions [A is in the $16d$ Wyckoff site with coordinates $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and the anion X is in the $8b$ site with coordinates $(\frac{3}{8}, \frac{3}{8}, \frac{3}{8})$] and the remaining O atoms are located in the $48f$ Wyckoff site with coordinates $(x, \frac{1}{8}, \frac{1}{8})$. As shown by Subramanian (Subramanian *et al.*, 1983), in this structure the A cation has eightfold coordination into a scalenohedron (distorted cube) and the B cation has sixfold coordination into a trigonal antiprism (distorted octahedron). The oxygen independent parameter x defines the distortion of the A and B polyhedra coordination. Geometrically, when $x = 0.3125$ the BO_6 polyhedron is a regular octahedron while the AO_8 polyhedron is a distorted cube (scalenohedron); for $x = 0.375$, the AO_8 polyhedron is an ideal cube and BO_6 is a distorted octahedron. Thus, the octahedron and the cube cannot both be regular. Furthermore, the limiting value for these compounds to become fluorites is $x > 0.375$. Usually, the x parameter lies between 0.309 and 0.355 and these values imply distorted cubes and octahedra simultaneously (Subramanian *et al.*, 1983). Therefore, the Isupov’s assumption is hardly achieved in pyrochlore structure leading to incoherent tolerance factor calculations.

To consider the effect of essential structural features on the tolerance factor, Cai *et al.* (2011) recently proposed two tolerance factors to describe the pyrochlore crystal structure. Cai *et al.* considered the geometrical features of the different cation coordination polyhedra and proposed two distinct tolerance factors

$$t_1 = \frac{[(x - \frac{1}{4})^2 + \frac{1}{32}]^{1/2} (R_A + R_O)}{[(x - \frac{1}{2})^2 + \frac{1}{32}]^{1/2} (R_B + R_O)} \quad (3)$$

and

$$t_2 = a \frac{3^{1/2}}{[8(R_A + R_O)]}. \quad (4)$$

The t_1 and t_2 parameters proposed by Cai *et al.* are tolerance factors corresponding to A_2B_2 and XA_4 polyhedra, respectively. In the first one the O anion is present, while in the second it is the X anion. Mainly based on the t_1 parameter, Cai *et al.* proposed a stability field to distinguish pyrochlores from weberites (fluorite-related structures). A relationship between the tolerance factors and dielectric properties and their applicability to analyze structure–property relations was discussed. However, both defined tolerance factors depend either on the cubic lattice parameter or on independent oxygen position parameters. The introduction of these structural parameters makes the tolerance factors proposed by Cai *et al.* more precise, but this complicates their calculations, because, as pointed out by Cai *et al.*, it is necessary to measure a and x data prior to their calculation. Although we can use

theoretical estimates based on the Nikiforov (1972) and bond-valence sum methods (Brown, 2006) for these parameters, this greatly limits the structural predictions for pyrochlore compounds. Therefore, an empirical tolerance factor that does not depend on the structural parameters, just on the ionic radii, is proposed in this work.

3. New empirical tolerance factor for pyrochlore structure

As discussed, the main goal is to obtain an expression for the tolerance factor for pyrochlores similar to that proposed by Goldschmidt for perovskites, which depends only on the ionic radii of the constituent ions. For this, we started from the expressions proposed by Cai *et al.* (2011). Therefore, we need to obtain either a or x as a function only of the ionic radii, in a manner that fits well into the available experimental data at room temperature and atmospheric pressure. However, to accurately model the x parameter, one would need to employ mainly neutron diffraction data, due to the well known difficulty of determining precise coordinates of light atoms, such as oxygen, by X-ray diffraction. Although this care avoids misleading results, it also reduces greatly the data amount that can be used in the fit. Thus, we started from the t_2 parameter and obtained an expression for the lattice constant.

Recently, Brik & Srivastava (2012) succeeded in predicting lattice constants for several pyrochlores. However, the expression proposed by them that depends only on the ionic radii is inadequate to model pyrochlores with mixed cations and anions. Thus, their main expression included not only ionic radii, but also electronegativities of the constituting ions, which is again undesirable for our purposes. So in this work we tested many forms of dependence of the lattice constant with

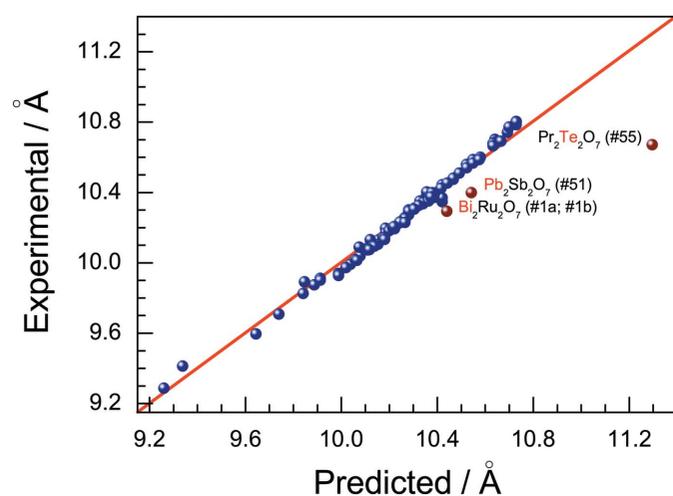


Figure 1

Comparison between the experimental and calculated lattice constants for pyrochlores. The red line is a guide for the eyes, representing the ideal case where the experimental and calculated values perfectly match. The red dark data points (labeled) correspond to the compounds containing an ion with a stereochemically active non-binding electron lone pair. The labels in parentheses refer to Tables 1, 2 and 3 of the supplementary material.

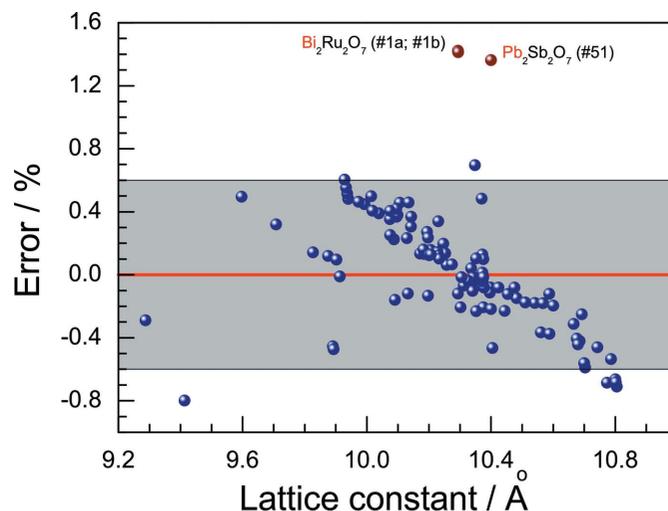


Figure 2

Percent errors between the calculated and experimental lattice constants. The light blue region encloses compounds for which the percent deviation is not greater than 0.6%. The red dark data points have the same meaning as in Fig. 1. Since the error for $\text{Pr}_2\text{Te}_2\text{O}_7$ was too large, it was not shown. Refer to Table 1 of the supplementary material for numerical values.

$R_A + R_O$ and $R_B + R_O$ for the same ternary pyrochlores used in Brik and Srivastava's work, being 79 distinct compounds in total.¹ In those cases of materials whose lattice parameters have more than one experimental value reported, all of them were considered, which leads to 110 different values. All the experimental data used are available as supplementary material, along with the corresponding ICSD (Inorganic Crystal Structure Database; Bergerhoff & Brown, 1987; Belsky *et al.*, 2002) reference for each lattice constant value.²

From all the expressions tested, the one that best fits the experimental data was

$$a = \frac{8}{3^{1/2}} \left[1.43373(R_A + R_O) - 0.42931 \frac{(R_A + R_O)^2}{R_B + R_O} \right], \quad (5)$$

where we took the oxygen ionic radius to be 1.38 Å. Comparison between the experimental and calculated lattice constants obtained is shown in Fig. 1, while the percent errors with respect to the experimental data are shown in Fig. 2. The data points marked in dark red correspond to compounds containing ions with a stereochemically active non-binding electron lone pair. These were not used in the fit, since in this case the concept of a spherical ion (implied by the assumption that it possesses an ionic radius) is not so good anymore. Besides, such lone pairs tend to repel the neighboring oxygen ions, distorting the structure and making it deviate from the expected structure. Accordingly, these compounds noticeably correspond to the most poorly reproduced values, as one can expect for a model based on spherical ions.

¹ We excluded theoretical values and measured values that were not taken at room temperature and atmospheric pressure.

² All the experimental and calculated values for the lattice constants, along with the experimental x parameters are available from the IUCr electronic archives (Reference: HW5025). Services for accessing these data are described at the back of the journal. employed ionic radii are available as supplementary material.

Now we compare our model for the lattice constant with the model of Brik and Srivastava. For the compounds considered here (see Table 1 in the supplementary material), both models provide a root-mean-square deviation between the calculated and experimental of $\sim 0.02 \text{ \AA}$, but our average percent error (0.27%) is subtly lower than theirs (0.41%).³ Except for three pyrochlores presenting the lone-pair effect [$\text{Pr}_2\text{Te}_2\text{O}_7$ (5.85%), $\text{Bi}_2\text{Ru}_2\text{O}_7$ (1.42%) and $\text{Pb}_2\text{Sb}_2\text{O}_7$ (1.36%)], the error does not exceed 1%; for six compounds the errors lie between 0.6 and 1%; all the remaining crystals have an error lower than 0.6%. Thus, we have a reliable prediction for the lattice parameter of the pyrochlores based uniquely on the ionic radii. The error predicting the lattice parameter by our model for the mixed pyrochlores cited by Brik & Srivastava (2012) is also subtly lower than the error they obtained. For those compounds the average percent error is 0.45% with a maximum value of 1.82%. Thus, we preferred to model the lattice parameter using equation (5) rather than that proposed by Brik & Srivastava (2012) that depends only on the ionic radii.

Finally, since we have established that equation (5) provides a very good estimate of the lattice constant for pyrochlores, we propose a new empirical equation for the tolerance factor for pyrochlore oxides compounds. Using the Cai *et al.* expression and substituting the obtained a value, we have

$$t = 1.43373 - 0.42931 \left(\frac{R_A + R_O}{R_B + R_O} \right). \quad (6)$$

We stress that the advantage of this expression lies in the absence of the explicit dependence on structural parameters (although it takes them into account), which allows us to predict structural and property features of pyrochlore compounds before measuring or modeling/estimating their structural data, as is the case for perovskites. Interestingly, the tolerance factor decreases with $[(R_A + R_O)/(R_B + R_O)]$, which is different from what has been proposed by Isupov for pyrochlores and by Goldsmith for perovskites. This suggests a limit value for the tolerance factor, because this cannot be negative or null.

The histogram that describes the pyrochlore distribution according to the new tolerance factor is shown in Fig. 3. We tested the distribution according to three normal distribution tests: Shapiro–Wilk, Lilliefors and Kolmogorov–Smirnov. For all, at the level of 0.05, the data was significantly drawn from a normally distributed population. Therefore, although the new tolerance factor was based on the t_2 tolerance factor proposed by Cai *et al.* (2011), the new distribution was symmetrically distributed. Thus, we fit the histogram with a Gaussian curve (shown in Fig. 3), whose centre occurs at the tolerance factor of $t = 0.913$. For pyrochlores with a tolerance factor near this value, the radii ratio R_A/R_B was near 1.6. This value makes sense since it is almost in the middle of the R_A/R_B range (1.46–1.80) proposed by Subramanian *et al.* (1983) as necessary for pyrochlore formation.

³ We considered the absolute values of the percent errors in order to avoid cancelations between positive and negative values.

4. Properties correlated to the new tolerance factor

One of the most important applications of tolerance factors is to estimate the structure stability field. Previously, Subramanian *et al.* (1983) reported for pyrochlores that the A and B ionic radii could be used to define the stability field for $A_2^{3+}B_2^{4+}O_7$, which was driven by the radii ratio, $(\frac{R_A}{R_B})$, and the independent oxygen coordinate, x . In their work Cai *et al.* (2011) used the tolerance factor t_1 to establish a stability field for pyrochlores, to mainly distinguish between weberites and pyrochlores structures. In this case they obtained a good stability field, with a separation between weberites and pyro-

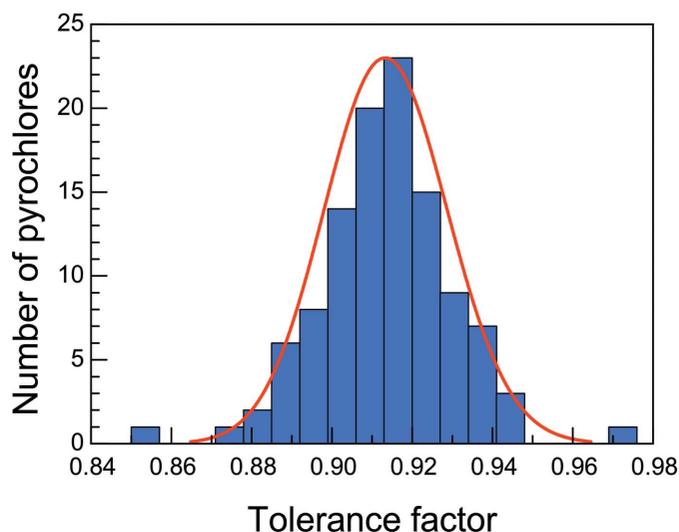


Figure 3
The distribution of pyrochlore compounds based on the new tolerance factor.

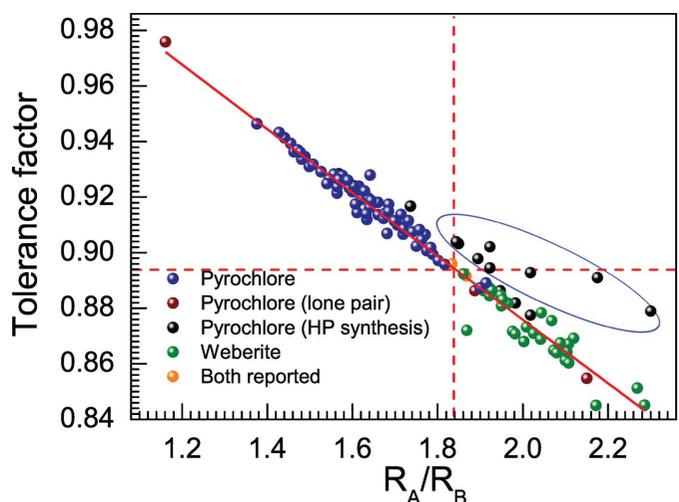


Figure 4
Tolerance factor as a function of the ionic radii of the A and B cations indicating the separation between weberite and pyrochlore structure. The vertical and horizontal red dashed lines indicate the best point to distinguish pyrochlores from weberites according to the radii ratio and tolerance factor. The red inclined line indicates a linear fit ($R^2 = 0.9704$), whose expression is $t = 1.1045 - 0.1143 \left(\frac{R_A}{R_B} \right)$.

chlores. However, due to the meaningless value of x for weberites, t_1 may not be the best way to distinguish pyrochlores and weberites according to the authors (Cai *et al.*, 2011). In Fig. 4 we plot the stability field based on the new tolerance factor for compounds with pyrochlore and weberite structures. From our stability field it is clear we distinguish between pyrochlores and weberites based just on the tolerance factor, as clear as the radii ratio and better than the one proposed by Cai *et al.* (2011). Note we do not have any problem with the absence of structural data for weberites because we need just the ionic radii.

The structural stability field for oxide pyrochlores was well described by Subramanian *et al.* using the cation radii ratio. We can see from Fig. 4 our tolerance factor defines a stability field similar to that defined by the radii ratio. As well as our tolerance factor, the radii ratio cannot differentiate weberites and pyrochlores synthesized at high pressures. However, when we use both together these parameters can predict the pyrochlores synthesized at high pressures, as indicated in Fig. 4 (see data inside the ellipse), which are obtained, preferentially, using radii ratio for weberites and tolerance factor for pyrochlores.

In perovskites, the most remarkable correlations between the tolerance factor and properties are associated with the phonons and dielectric constant. Fig. 5 shows for pyrochlore compounds with $B = \text{Sn}$ or Ti the behaviour with the tolerance factor of the highest IR-active mode experimentally observed, whose symmetry is F_{1u} . IR-active phonons are important, because they are directly connected to the dielectric constants. The behaviour demonstrates a strong correlation with the new tolerance factor, whose Pearson product–moment correlation coefficient is 0.97. For all remaining IR-active phonons an ionic mass dependence was observed when correlated with the tolerance factor. The mass effect is not observed for the highest phonon because in this vibration the A and B ions are almost stopped, being the motion associated mainly with the O

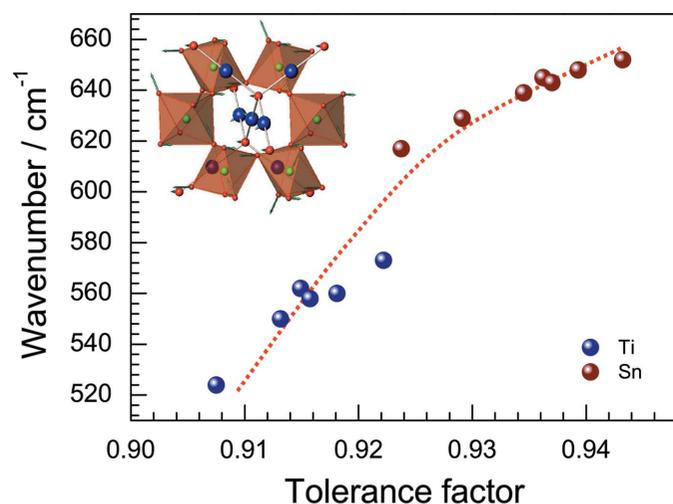


Figure 5
Correlation between the tolerance factor and the highest IR-active observed mode. The red dashed line is a guide for the eye. The inset shows the phonon vibration according to the force field proposed by Silva *et al.* (2013).

atoms in the octahedra (see inset in Fig. 5). The increasing behaviour can be explained considering the oxygen motion in this phonon. The motion changes linearly the $B\text{—O—}B$ angle, which changes linearly with the oxygen parameter x (Subramanian *et al.*, 1983). However, the x parameter increased with the tolerance factor for the considered B ions ($B = \text{Ti}$ and Sn), implying an increase of the wavenumber value when the tolerance factor increases. In fact, there is a small correlation (Pearson product–moment correlation coefficient of 0.65 when considering just parameters determined by neutron and synchrotron data) between the x parameter and the tolerance factor, as shown in Fig. 6. Observe that the oxygen parameter x exhibits a clear trend in its values as a function of tolerance factor, increasing when the tolerance factor increases.

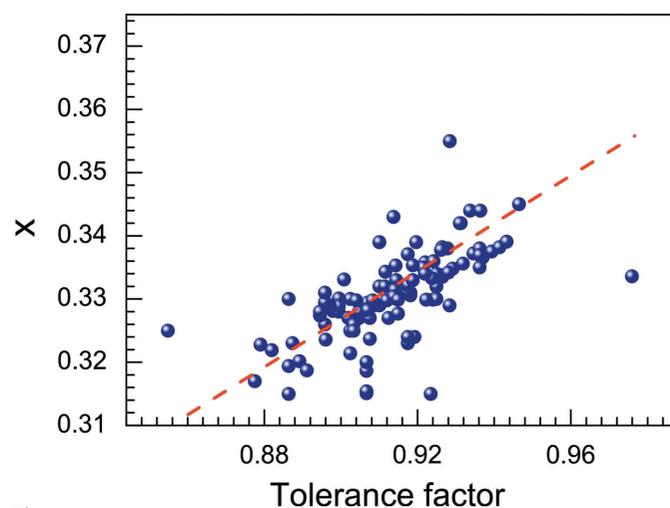


Figure 6
Correlation between the tolerance factor and the structural oxygen parameter x . The line indicates a linear fit ($x = -0.0147 + 0.3794t$) to indicate the trend. The scale of the y axis was chosen to show all possible x parameter values.

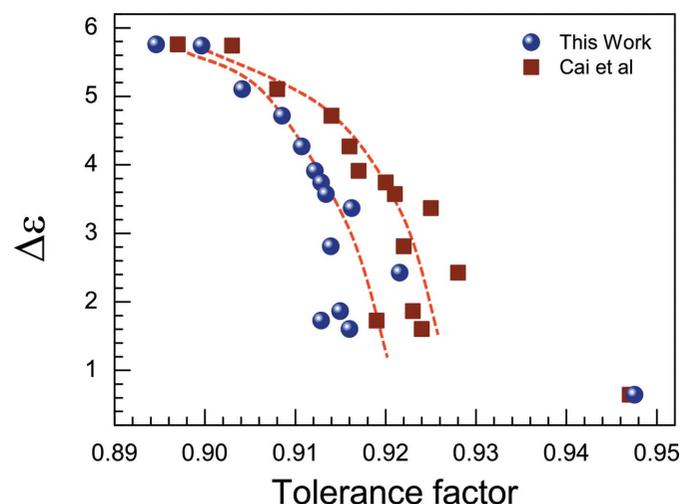


Figure 7
Normalized permittivity difference dependence with the tolerance factor. The values calculated by Cai *et al.* are also shown. The red dashed lines are guides for the eye. The compounds used in this figure are listed in Table 4 of the supplementary material.

Finally, we can show that our tolerance factor exhibits the same correlation as that proposed by Cai *et al.* (2011) for the normalized difference in dielectric permittivity $\Delta\varepsilon_n$, as shown in Fig. 7. This parameter is defined in terms of the measured dielectric constant ε_m , the permittivity obtained by the Clausius–Mossotti ε_r and the microscopic polarizability, α , as

$$\Delta\varepsilon_n = \frac{\varepsilon_m - \varepsilon_r}{\alpha}. \quad (7)$$

5. Conclusions

In summary, we have proposed an empirical tolerance factor for compounds with pyrochlore structure based only on the ionic radii of the constituent ions. The pyrochlore distribution according to the new tolerance factor is symmetrically centred at the value $t = 0.913$, which is an ideal value connected to the R_A/R_B ratio proposed by Subramanian *et al.* (1983) as necessary for pyrochlore formation. The new tolerance factor permits a good prediction of the lattice parameter and exhibits a strong correlation with several properties, such as those related to the stability, phonons and dielectric constants.

6. Related literature

All the experimental data used to model the lattice parameter were obtained from: Kanno *et al.* (1993), Abraham *et al.* (1975), Lewandowski *et al.* (1992), von Gaertner (1930), Munenaka & Sato (2006), Gasperin (1955), Lukaszewicz *et al.* (1994), Brisse *et al.* (1972), Jona *et al.* (1955), Reading & Weller (2001), Wang & Sleight (1998), Mizoguchi *et al.* (2004), Kennedy (1996), Muller *et al.* (1964), Haghhighirad, Gross & Assmus (2008), Subramanian *et al.* (1988), Taira *et al.* (2003), Tabira *et al.* (2000), Knop *et al.* (1968), Chien & Sleight (1978), Millican *et al.* (2007), Bertaut *et al.* (1959), Douma *et al.* (2010), Chtoun *et al.* (2001), Apetrei *et al.* (2007), Kobayashi *et al.* (1995), Kennedy *et al.* (1997), Mandal *et al.* (2007), Klein *et al.* (2007), Sidey *et al.* (2008), Bansal *et al.* (2002), Shimakawa *et al.* (1999), Reid *et al.* (1977), Whittle *et al.* (2009), Brisse *et al.* (1968), Kumar *et al.* (2010), Tabira *et al.* (2001), Deiseroth & Mueller Buschbaum (1970), Harvey *et al.* (2005), Knoke *et al.* (2006), Haghhighirad, Ritter & Assmus (2008), Soderholm *et al.* (1982), Greedan *et al.* (1996), Zabel *et al.* (1997), Kennedy & Vogt (1996), Yamamoto *et al.* (1994), Kimmel *et al.* (2007), van Dijk *et al.* (1984), Mandal *et al.* (2010), Zouari *et al.* (2009), Weber & Schleid (2000), Pontonnier *et al.* (1992), Subramanian *et al.* (1996), Hoekstra & Siegel (1968), Reimers *et al.* (1988), Kennedy (1995), Facer *et al.* (1993), Matteucci *et al.* (2007), Shlyakhtina *et al.* (2009).

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