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Getting more out of $X_2T_2O_7$ compounds with thortveitite structure: The bond-valence model

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Abstract

C-$M_2Si_2O_7$ (M = RE and In) and crystals of composition $X_2T_2O_7$ (T = P, As, Ge) with ionic radius of X less than 0.97 Å (X = Ni, Cd, Mg, Zn, Cu, Ca) are isostructural with the natural-occurring mineral thortveitite. In those compounds, the T–O bridging distance values vary considerably and there is no explanation to this fact in the literature. This paper will bring their structural characteristics out by the bond-valence model. It has been concluded that T–O bridging distance and mean T–O distance are linearly correlated to the total atomic valence of the bridging oxygen and the T atom (T = Si, P, As, Ge), respectively, and they are a function of the principal quantum number (n) in the valence shell of the atom T. Finally, we have applied successfully the model for the prediction of Ge–O distances of $(In,A)_2Ge_2O_7$ (A = Fe,Y,Gd) compounds.
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Keywords: Solid state; Bond-valence model; Silicate

1. Introduction

C-$M_2Si_2O_7$ (M = rare earth and In) and crystals of composition $X_2T_2O_7$ (T = P, As, Ge) with ionic radius of X less than 0.97 Å (X = Ni, Cd, Mg, Zn, Cu, Ca) are isostructural with the natural-occurring mineral thortveitite ($Sc_2Si_2O_7$) [1]. It crystallizes in the monoclinic system, with space group $C2/m$. Fig. 1a shows the thortveitite unit cell, which consists of a single crystallographic Si site and a single Sc site. The structure can be described as a close hexagonal packing of the oxygens with Sc^{3+} cations in octahedral holes and silicon in tetrahedral holes in alternating parallel layers (001). The diortho groups Si_2O_7 show a Si–O–Si bond angle of 180° and the (SiO_4) tetrahedra show a very low degree of distortion as compared to other disilicate configurations. There are two kinds of oxygens in the thortveitite structure (Fig. 1b). One is a bridging (br) oxygen connecting the silicon atoms into a dimmer and the other is a non-bridging (nbr) oxygen. The co-ordination numbers of the bridging and non-bridging oxygens are two and three, respectively.

The Si–O–Si bond angle of 180°, typical of the thortveitite structure, deserves special attention because this value is unusual with respect to most other sorosilicates where the corresponding angles are definitely smaller (130–140°) [2]. However, this configuration provides a wide range of stability that makes the C-$RE_2Si_2O_7$ (RE = rare earth) polymorph the only one of the family of disilicate structures which is stable from room temperature up to the melting point.

Table 1 shows structural data (mean Si–O distance, Si–O(br) distance and Si–O(nbr) distance) of the C-$M_2Si_2O_7$ compounds found in the literature [3–8]. All data correspond to single crystal structural refinements except that of C-$Er_2Si_2O_7$, whose structure has only been refined from powder data, to our knowledge. The structural data of $X_2T_2O_7$ (T = P, As, Ge) isostructural with thortveitite [1,9–16] have been included in Table 2. Table 1 shows that the Si–O(br) distance is shorter than the Si–O(nbr) distances in thortveitite ($Sc_2Si_2O_7$) but this is not the case for all C-$M_2Si_2O_7$ and $X_2T_2O_7$ compounds, as observed in Tables 1 and 2.

The configuration of the (Si_2O_7) double-tetrahedra groups in thortveitite-type structure is of special interest and it has been studied from several points of view. Brown

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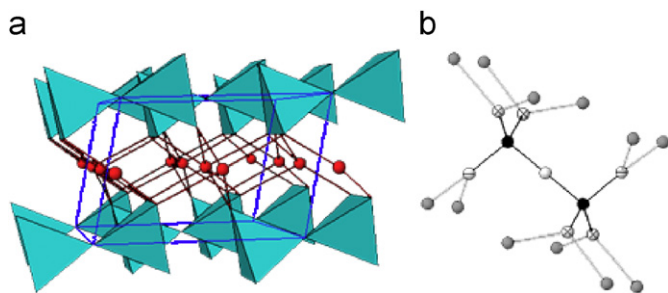 E-mail address: alba@icmse.csic.es (M.D. Alba).

Fig. 1. Crystal structure of thortveitite, C-$M_2Si_2O_7$. (a) SiO_4 tetrahedra and Sc^{3+} cations bonded to the non-bridging oxygens. (b) Coordination of the O(br) and O(nbr). Black spheres: Si; crossed spheres: O(nbr); white sphere: O(br) and gray sphere: Sc.

Table 1
Mean Si–O distance, Si–O(br) distance and Si–O(nbr) distance in C-$M_2Si_2O_7$

$M_2Si_2O_7$	Mean Si–O distance (Å)	Si–O(br) distance (Å)	Si–O(nbr) distance (Å)	References
$In_2Si_2O_7$	1.625	1.608	1.631	Patzke et al. [3]
$Sc_2Si_2O_7$	1.624	1.606	1.630	Smolin et al. [4]
$Y_2Si_2O_7$	1.627	1.628	1.626	Redhammer and Roth [5]
$Er_2Si_2O_7$	1.635	1.645	1.631	Christensen [6]
$Yb_2Si_2O_7$	1.626	1.626	1.626	Smolin and Shepelev [7]
$Lu_2Si_2O_7$	1.625	1.622	1.626	Soetebier and Urland [8]

Table 2
Mean T–O distance, T–O(br) distance and T–O(nbr) distance in C-$M_2T_2O_7$

$M_2T_2O_7$	Mean T–O distance (Å)	T–O(br) distance (Å)	T–O(nbr) distance (Å)	References
$In_2Ge_2O_7$	1.737	1.703	1.749	Pfeifer et al. [9]
$Mg_2P_2O_7$	1.560	1.557	1.561	Calvo [10]
$Cu_2P_2O_7$	1.517	1.543	1.508	Robertson and Calvo [11]
$Zn_2P_2O_7$	1.557	1.569	1.553	Calvo [12]
$Ni_2P_2O_7$	1.536	1.500	1.547	Pietraszko and Lukaszewick [13]
$Mg_2As_2O_7$	1.700	1.712	1.695	Lukaszewick [14]
$Ni_2As_2O_7$	1.672	1.647	1.680	Buckley et al. [1]
$Ca_2As_2O_7$	1.673	1.712	1.660	Pertlink [15]
$Cd_2As_2O_7$	1.676	1.704	1.667	Weil [16]

and Calvo [17] have studied the systematic of all possible double-tetrahedra configurations of anions $(X_2O_7)^{-n}$ and the packing with a certain number of individual cations providing charge balance. Other analyzed aspect is that the (Si_2O_7) configuration is apparently determined by the bonding and polarizing forces of the surrounding cations. Thus, any periodicity of the rare-earth electronic structures, such as variation in ionic size or electronegativity,

along the series of trivalent rare earths, should be reflected in the changing configuration of the (Si_2O_7) double tetrahedra. A third aspect studied involves the double π-bonding theory for $(XO_4)^{-n}$ tetrahedra ions ($X = $ Si, P, S, Cl), developed by Cruickshank [18], which can provide much useful information for the discussion of the bonding lengths and angles observed in (Si_2O_7) groups in rare-earth disilicate structures. On the one hand, the interatomic mean Si–O distances in the majority of the rare-earth disilicates are shorter than 1.63 Å, which is smaller than the sum of the covalent radii of Si and O (1.83 Å) and than the expected Si–O bond length allowing for correlations associated with the difference in electronegativity (1.76 Å).

There are many studies devoted to understanding variations in Si–O bond length in silicates [19–24], but no unequivocal correlation between d(Si–O) and other structural or electronic parameters has been found. Ohashi [25] has shown that the Si–O(br) distance in siloxanes directly correlates with the electronegativities of the substituents. Fig. 2 shows a plot of the T–O(br) distance values in $X_2T_2O_7$, with $T = $ Si, P, As, versus the Pauling electronegativity values of the X atoms [26]. The scattering of the data denotes that the T–O(br) distance in those compounds cannot be interpreted by the use of the simple model employed in siloxanes but other factors have to be taken into account.

The aim of this work is to rationalize the observed differences in the mean T–O and the T–O(br) distances in the different $X_2T_2O_7$ compounds, with $T = $ Si, Ge, P, As, isostructural with thortveitite under the bond-valence theory.

2. Results and discussion

The bond-valence model [27,28] provides a useful and quantitative description of inorganic bonding. In this model, all neighboring cation–anion distances are considered to be bonds although not all of them of equal strength. In inorganic compounds the total atomic valence of atom i, V_i, is defined by

$$V_i = \sum_j \exp\left[(r_o - r_{ij})/0.37\right] \tag{1}$$

for all atoms j bonded to the atom i, where r_{ij} (in angstroms) is the oxygen-cation bond length as determined by crystal structure analysis and r_o is the empirically derived length of an oxygen-cation bond of unit valence [29].

We have calculated the total atomic valence of the bridging oxygen for each $X_2T_2O_7$ compound by using the T–O(br) distances reported in Tables 1 and 2 and a value of $r_o = 1.624$ Å for the O–Si bond, $r_o = 1.767$ Å for the O–As bond, $r_o = 1.617$ Å for the O–P bond and $r_o = 1.748$ Å for the O–Ge bond [29]. Fig. 3 is a plot of the T–O(br) distances versus the total atomic valence of the bridging oxygen. Two linear correlations, with very similar slopes, are observed, one comprising those $X_2T_2O_7$ compounds
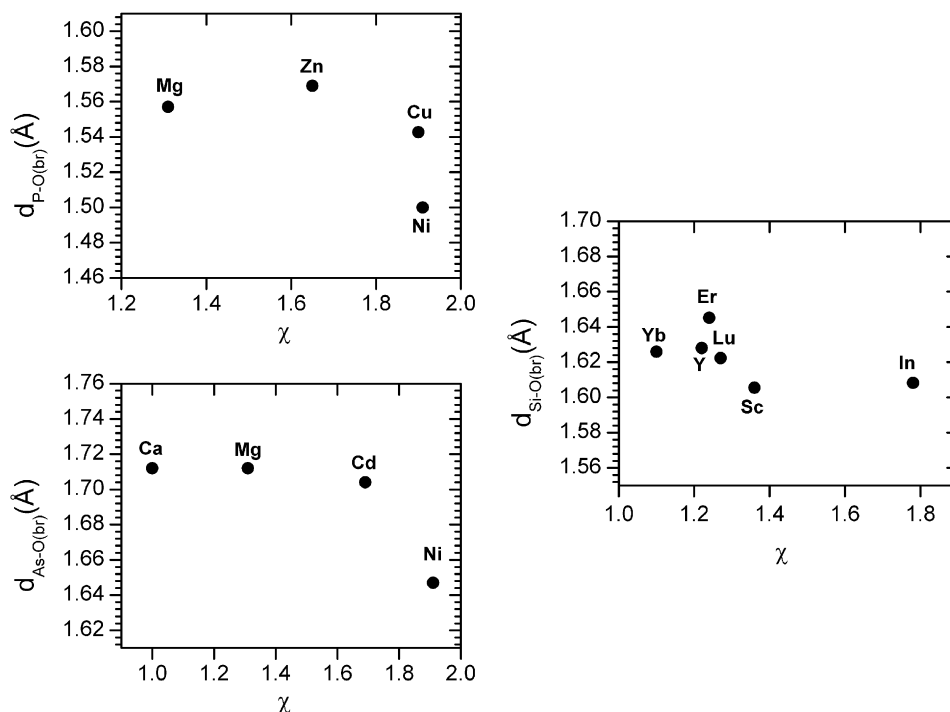
Fig. 2. T–O(br) distance in $X_2T_2O_7$ (T = Si, P, As) versus the Pauling electronegativity of the X atom.
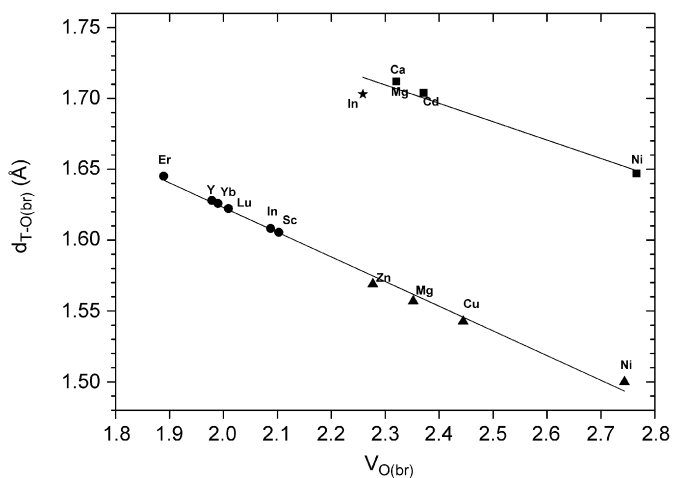

Fig. 3. T–O(br) distance in $X_2T_2O_7$ (T = Si, P, Ge, As) versus the oxidation state of bridge oxygen. circles: $X_2Si_2O_7$; triangles: $X_2P_2O_7$; star: $X_2Ge_2O_7$; squares: $X_2As_2O_7$; solid line: the calculated values from Eq. (3).
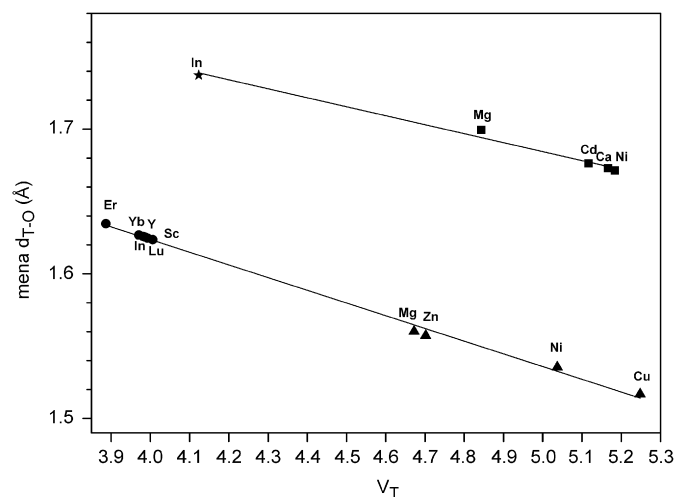

Fig. 4. Mean T–O distance in $X_2T_2O_7$ (T = Si, P, Ge, As) versus the oxidation state of T. circles: $X_2Si_2O_7$; triangles: $X_2P_2O_7$; star: $X_2Ge_2O_7$; squares: $X_2As_2O_7$; solid line: the calculated values from Eq. (4).

with T (T = Si, P) belonging to the third period of the periodic table and the other comprising the $X_2T_2O_7$ compounds with T (T = Ge, As) belonging to the fourth period of the periodic table. Therefore, the T–O(br) distances in thortveitite type compounds depend linearly on the total atomic valence of the bridging oxygen, as predicted by the bond-valence model, but they are modulated, in turn, by the principal quantum number (n) of the valence shell of the T atom. Moreover, it is observed that as the total atomic valence of the bridging oxygen increases, the T–O(br) bond distance decreases as a consequence of an increase in the bonding strength. A

general expression for the calculation of T–O(br) distance in $X_2T_2O_7$ compounds with thortveitite structure is given by

$$d_{T-O(br)} = 1.8607 + 0.0368 \times n - (0.3071 - 0.0443 \times n) \times V_{O(br)}. \qquad (2)$$

In Fig. 3, we have also included the theoretical line calculated by using Eq. (2). For 15 different $X_2T_2O_7$ compounds, a high correlation ($R^2 = 0.994$) between the experimental T–O(br) distance and those predicted by using this equation is observed, the maximum deviation

between experimental and theoretical T–O(br) distance is 0.006 Å for $n = 3$ and 0.012 Å for $n = 4$. We believe that this result indicates considerable potential for the approach in predicting T–O(br) distances in such structure and others related. The total atomic valence of the T atoms, V_T, can be calculated through Eq. (1), taking into account that there are three different crystallographic sites for oxygen in $X_2T_2O_7$. Fig. 4 is a plot of the mean T–O distances (including bridging and non-bridging oxygens) and the total atomic valence of the atom in tetrahedral coordination (T). As observed in the former case for the bridging oxygen, the relation between V_T and d_{T-O} shows two sets of linear correlations, one comprising $X_2T_2O_7$ with T belonging to the third period of the periodic table and the other comprising those $X_2T_2O_7$ with T belonging to the fourth period of the periodic table. It is observed that as the total atomic valence of the atom in tetrahedral

coordination (T) increases the mean T–O bond distance decreases as a consequence of an increase in the bonding strength. However, both the origin and the slope of the linear regression are a function of the principal quantum number (n) of the valence shell of the atom T. A general expression for the calculation of the mean T–O distance in the $X_2T_2O_7$ compounds with thortveitite structure is as follows:

$$d_{T-O} = 1.9141 + 0.0202 \times n - (0.1648 - 0.0257 \times n) \times V_T. \tag{3}$$

In Fig. 4, we have also included the theoretical line calculated by using Eq. (3). For 15 different $X_2T_2O_7$ compounds, a high correlation ($R^2 = 0.988$) between mean T–O distance and those predicted by using this equation is observed, the maximum deviation between the experimental and theoretical mean T–O distances being 0.005 Å for

Table 3
Comparison between observed and predicted Ge–O distances for $(In,A)_2Ge_2O_7$

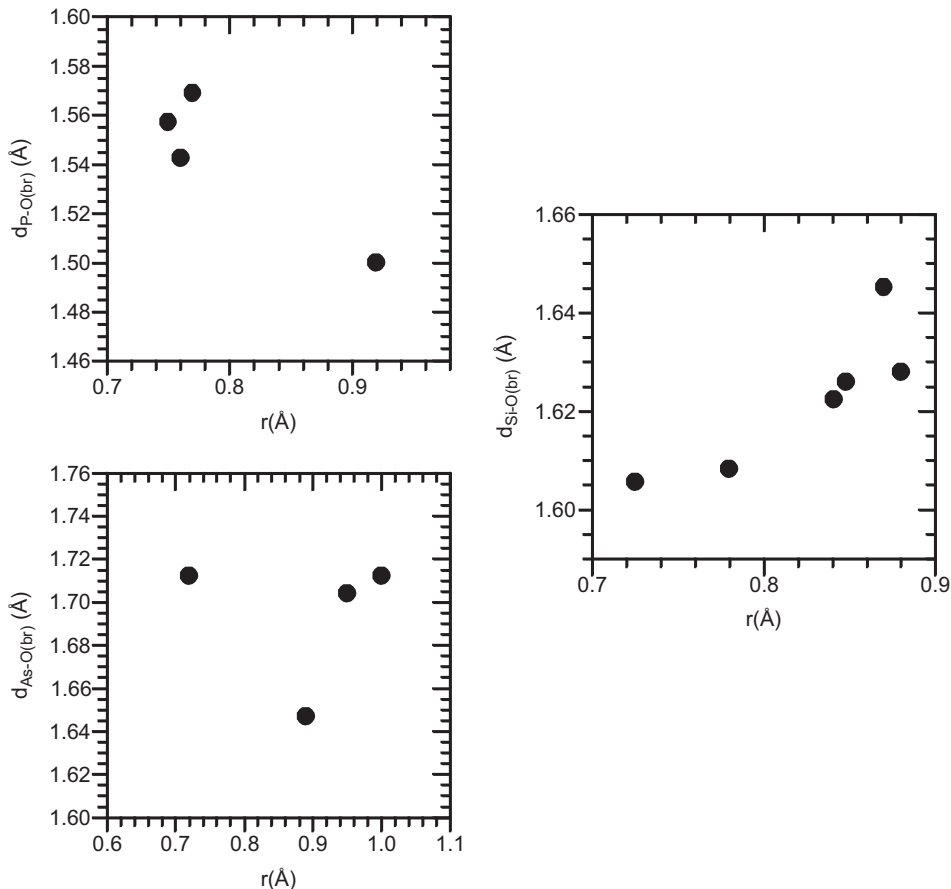| $(In,A)_2Ge_2O_7$	Ge–O$_{(br)}$ obs. (Å)	Ge–O$_{(br)}$ calc. (Å)	Error (Å)	Mean Ge–O obs. (Å)	Mean Ge–O calc. (Å)	Error (Å)
$In_{1.08}Gd_{0.92}Ge_2O_7$	1.704	1.714	0.010	1.698	1.710	0.012
$In_{1.12}Y_{0.88}Ge_2O_7$	1.708	1.718	0.010	1.728	1.732	0.004
$In_{1.07}Fe_{0.93}Ge_2O_7$	1.698	1.710	0.012	1.706	1.716	0.010

Fig. 5. T–O(br) distance in $X_2T_2O_7$ (T = Si, P, As) versus the ionic radii of the X atom.

$n = 3$ and 0.010 Å for $n = 4$. We believe that this result indicates considerable potential for the approach in predicting mean T–O distances in such structure and others related.

Finally, we will demonstrate the utility of the method for predicting Ge–O distances in solid solutions with the following compositions: $(In,A)_2Ge_2O_7$ $(A = Fe,Y,Gd)$ [30–32]. We have calculated the total atomic valence of the bridging oxygen and of the Ge atom and we have applied the Eqs. (2) and (3) for the calculation of the Ge–O(br) and mean Ge–O distances. Table 3 shows the comparison between the observed and predicted values; the absolute errors are similar to those shown above for the $X_2T_2O_7$ compounds. Taking into account that there is no correlation between the mean radii of X and the T–O(br) distance (Fig. 5), it is predictable that the calculation of distance of those compounds thorough extrapolation between the structures of the end members using the mean ionic radius will fail.

3. Concluding remarks

We have demonstrated the general application of the bond-valence model to the $X_2Y_2O_7$ $(Y =$ Si, P, As, Ge) isostructural with thortveitite and the general expressions for the calculation of the mean T–O distance and T–O(br) distance in this compounds have been proposed.

Both structural parameters, T–O(br) and mean T–O distances, are linearly correlated to the total atomic valence of the bridging oxygen and the atom in tetrahedral coordination (T), respectively, but they are modulated, in turn, by the principal quantum number (n) of the valence shell of the T atom. Eqs. (2) and (3) imply a modification of the general expression of bond-valence model by taking into account the influence of the principal quantum number. Previously, it was demonstrated by Mooser and Pearson [33] that the principal quantum number is a fundamental parameter to explain the structure of those compounds where the radius ratio rules were unsatisfactory.

Finally, we have applied successfully the model for the prediction of Ge–O distances of $(In,A)_2Ge_2O_7$ $(A = Fe,Y,Gd)$ compounds.

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