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Journal of Solid State Chemistry 179 (2006) 3429–3436

JOURNAL OF SOLID STATE CHEMISTRY

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A computational study into the (tetrahedral) distortion of TX_2 α-quartz materials: The effect of changing the chemical composition away from SiO_2

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Received 20 March 2006; received in revised form 20 June 2006; accepted 2 July 2006
Available online 16 July 2006

Abstract

We report a periodic density functional study into the tetrahedral distortion of a range of quartz-like TX_2 materials. The total tetrahedral distortion and its most sizable contribution, the angular part (angular tetrahedral distortion), are found to be strongly dependent on the chemical composition and to increase in the order of $BeF_2 < SiO_2 < CO_2 < GeO_2 < SiS_2 < GeS_2$. The bond stretching contribution to the total tetrahedral distortion appears to be significantly smaller and to vary more erratically with changes in the chemical composition. The sulphide materials in the study were found to have tetrahedral distortion values commonly associated in silica with experimentally unrealizable hypothetical frameworks, suggesting that such frameworks might become realizable when stepping away from silica. None of the tetrahedra were found to be strictly regular, in line with the analysis of Smith [Acta. Cryst. 16 (1963) 542–545], demonstrating that regular tetrahedra are in principle possible in quartz but that distortions from ideality are energetically advantageous. The energetic reason for this distortion is still an open question; we propose a simple electrostatic model that explains the ease with which tetrahedra can be distorted in terms of charge transfer and the relative charge on the X (O,S,F) atom.

Keywords: Quartz; Zeolite; Silica; Germania; Chalcogenide; Distortion; Tetrahedral distortion; Hypothetical frameworks; DFT

1. Introduction

Knowledge of the distortion of tetrahedral TX_2 frameworks (i.e., based on corner-sharing tetrahedra), both in terms of their tetrahedra (intratetrahedral) and the (intertetrahedral) linkages between them, is key to understanding the energetic ordering of different polymorphs and the nature of the phase transitions between them. For instance, we recently demonstrated that some hypothetical tetrahedral SiO_2 frameworks, which lie much higher in energy than their synthesized counterparts, typically have tetrahedra that also are much more distorted than those in synthesized materials [1]. We also showed that the energy difference between these hypothetical frameworks and the synthesized ones can most likely be attributed to the increased tetrahedral distortion. Philippot et al. [2,3] have furthermore demonstrated that mildly distorted α-quartz materials (e.g., SiO_2 quartz) undergo a displacive $\alpha \rightarrow \beta$ transition with increasing temperature, while more distorted α-quartz materials (e.g., GeO_2 quartz) instead undergo reconstructive transitions into other frameworks such as cristobalite.

Traditionally most (experimental) work has focussed on siliceous and metal phosphate (e.g., $AlPO_4$ and $FePO_4$) materials, due to their relevance as microporous zeotype frameworks and piezoelectric materials, but in recent years new classes of tetrahedral materials with different chemical composition have gained importance, for example chalgogenides [4–8], phosphorus nitride imide (HPN_2) [9,10], phosphorus oxynitride [11–14], beryllium fluoride [15] and carbon dioxide [16–18] based frameworks. While in

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doi:10.1016/j.jssc.2006.07.011

principle we could obtain information about the intra- and intertetrahedral distortion in such materials from an analysis of the available experimental data, any direct comparative analysis is severely hindered by the fact that there is no single framework type which all these compositions are known to adopt, as well as the small number of statistically significant figures in the experimentally obtained crystallographic data compared to the magnitude of distortions. Therefore, we chose instead to employ density functional calculations to obtain consistent structural data for a range of chemical compositions and frameworks, thereby extending the framework type/composition range to include materials which are either not yet synthesized or hitherto not completely characterized (e.g., CO_2), and to use these structures as input for a subsequent analysis of the tetrahedral distortion. Where possible, we verified the structures obtained against experimental data. To avoid the uncertainties associated with crystallographic disorder, here we concentrate on binary materials with the simple TX_2 stoichiometry. In this communication we report the first results of this study, specifically focussing on the changes in the tetrahedral distortion of quartz-like materials associated with changes in chemical composition. More specifically, we study the effect of replacing silicon and oxygen in SiO_2 quartz with neighbouring elements in their group, i.e., carbon and germanium for silicon and sulphur for oxygen. We further also compare SiO_2 quartz with its (formally) $T^{II}X^{I}_2$ equivalent BeF_2 quartz.

Historically speaking, it was once customary to assume that the tetrahedra in α-quartz and other silica phases were strictly regular; i.e.,, that all the deviations away from ideal geometries were the result of experimental errors and uncertainties. In 1963, however, Smith pointed out that for α-quartz the atomic positions in the unit cell are generated by a 3-fold screw axis, which is not a symmetry element of a tetrahedron, and that therefore the tetrahedra in α-quartz can be strictly regular only for very specific c/a values and T–X bond lengths [19]. Using experimental crystallographic data he further showed that the tetrahedra in both SiO_2 and GeO_2 α-quartz phases are consequently unlikely to be strictly regular, while those in the fluoride BeF_2 may possibly be. Further experimental studies by Philippot et al. on both TX_2 and $T^{III}T^{V}X_4$ (e.g., $AlPO_4$) synthesized α-quartz materials showed that the distortion of the tetrahedra is genuine and appears to vary linearly with the average T–X–T angle [3]. The distortion of tetrahedra in the quartz structure is thus strongly linked to, and constrained by, the unit-cell parameters and T–X bond lengths (see Fig. 1 for an overview of the possible distortions in quartz). This is true for all tetrahedral frameworks, albeit that the rigidity of constraints varies from framework to framework. The cristobalite and AST zeolite frameworks, for instance, are known to support strictly regular tetrahedra with the presence of linear T–X–T bond angles as the only constraint. This situation does not occur in practice, most likely because of the energetic cost associated with the straightening of the T–X–T linkages.

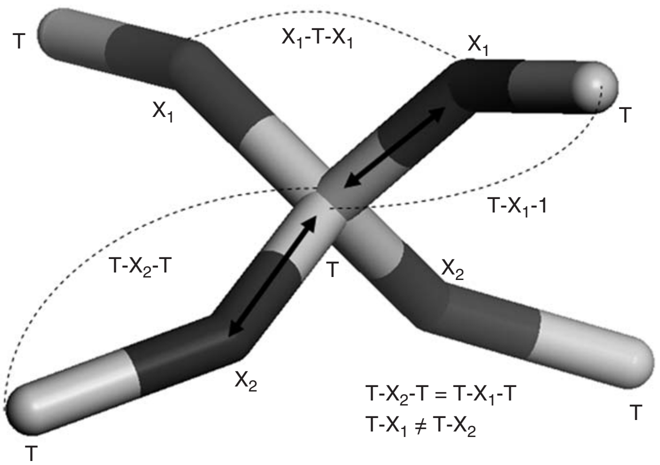

Fig. 1. Fragment of the quartz structure showing the possibilities for inter- and intratetrahedral distortion. The intertetrahedral distortion is related to the change in the T–X–T angle, while the intratetrahedral distortion (total tetrahedral distortion) originates from changes in the two independent T–X bond lengths (bold arrows, bond stretching tetrahedral distortion) and the four independent X–T–X angles (angular tetrahedral distortion). For sake of clarity only one of the six X–T–X angles (X_1–T–X_1) is shown.

The displacive phase transition between α-quartz and the idealized high-symmetry structure of β-quartz can be described as a simultaneous tilt of all the TX_4 tetrahedra in the unit-cell through a tilt angle δ, as defined by Grimm and Dorner [20]. This tilt angle is defined as zero for β-quartz and is non-zero for α-quartz structures. The value of δ is typically used as a measure of intertetrahedral distortion, away from the high symmetry β-quartz structure, as a function of chemical composition, although it is only rigorously defined in the context of a temperature driven $\alpha \rightarrow \beta$ transition of a model system of rigid tetrahedra. In the latter case, the T–X–T bond angle is a simple function of δ, but there is experimental evidence that this relationship also holds for systems with distorted tetrahedra.

2. Computational details

The six quartz-structured compounds discussed in the paper have been investigated with periodic density functional calculations, employing the CRYSTAL03 code [21] and the B3LYP hybrid exchange functional [22]. The basis set is composed of localized atomic orbitals, expressed in a series of Gaussian type functions. All the basis sets employed are available via the online library of the code [23] (Si [24], Ge [25], Be [26], O [24], S [27] F [28]); they are of double valence plus polarization quality for each atomic species. All elements are treated at the all-electron level.

We used a Monkhorst-Pack shrinking factor of 6, and truncation thresholds of (7 7 7 7 14) for the Coulomb and exchange series [21], while SCF convergence thresholds were set to 10^{-7} Hartree for both eigenvalues and total energies. These tolerances ensure high numerical accuracy in the calculations.

Geometry optimizations have been checked against the root-mean-square (RMS) and absolute value of the largest component for both gradients and nuclear displacements. Optimization was considered complete when the four conditions were simultaneously satisfied for both fractional coordinates and unit cell parameters, using the tight values of 12×10^{-5} for the maximum gradient and 18×10^{-5} for the maximum displacement (all in a.u.).

Wells and co-workers have recently developed a geometric analysis method and computer code (GASP) that calculates the tetrahedral distortion between the TX_4 units of a given framework and an ideal tetrahedron [29,30]. This distortion, expressed in terms of the RMS length of the vectors linking the X atom positions of the tetrahedra in the calculated quartz structures and their idealization, is a measure of the tetrahedral distortion and can be separated into two contributions which evaluate respectively the dilation and the rotation required to overlap the real and ideal X atom positions. We refer to the latter contribution as the *angular tetrahedral distortion* and to the dilation contribution as the *bond-stretching distortion*. The advantage of using such a scheme for analysing the tetrahedral distortion is that both contributions are treated on an equal footing (as RMS vector lengths) and expressed in the same length unit. The reference bond length for the bond stretching tetrahedral distortion is chosen to be equal to the RMS bond length of the structure in question and the bond stretching distortion is zero if all four T–X bonds have the same length. We employed GASP to calculate the tetrahedral distortions of all the frameworks considered, while all other structural parameters (with the exception of the tilt angle) were obtained using the ZeoTsites code from Sastre and Gale [31,32]. Finally, the tilt angle δ was calculated from the unit-cell parameters and the fractional coordinates of the X-atom using the equation given in [33].

3. Results and discussion

The calculated structural and electronic data (unit-cell dimensions, c/a ratio, average T–X bond length, average T–X–T angle, tilt angle, angular tetrahedral distortion, bond stretching tetrahedral distortion) for the six quartz materials studied are summarized in Table 1. The first observation is that for the three experimentally characterized materials (SiO_2, GeO_2 and BeF_2) the difference between the calculated and experimental [34] structural data is typically smaller than 2% and that the unit-cell dimensions, unit-cell volume and bond lengths are all slightly overestimated. This is a common feature of the B3LYP functional, which for crystalline materials slightly overestimates bond lengths and unit-cell volumes, as already discussed in the literature for SiO_2 [35]. The differences between the tetrahedral distortion calculated from experimental and DFT optimized structures is larger, most likely because of the small number of statistically significant figures in the experimental crystallographic date compared to the magnitude of the distortions involved (especially for the bond-stretching tetrahedral distortion), but both data sets show the same trends. Fig. 2 shows the change in c/a ratio with the average T–X–T angle for the quartz materials included in this study. As in the experimental studies by Philippot et al., we observe a linear trend over the whole range of values, where the c/a ratio decreases with increasing average T–X–T angle. For the tilt angle δ we find a similar correlation with c/a increasing with increasing tilt angle (not shown). Even though the hybrid B3LYP functional was optimized to reproduce molecular thermochemistry and it is not the optimal choice for crystalline solids [36], our DFT calculations with the B3LYP functional reproduce the experimental trends and thus capture the essential physics and chemistry at play in the tetrahedral distortion. They can therefore be employed reliably in the current study.

Comparing the angular, bond stretching and total tetrahedral distortion values given in Table 1 strongly suggests that the tetrahedral distortion of quartz is dominated by its angular contribution. The bond stretching tetrahedral distortion is between 2.5 and 55 times smaller than the angular tetrahedral distortion so that the total tetrahedral distortion correlates very strongly with the angular tetrahedral distortion ($R^2 = 0.998$ for the six

Table 1

Calculated structural and electronic parameters for the six quartz materials studied (where AT dist = angular tetrahedral distortion, BST dist = bond stretching tetrahedral distortion, TT dist = total tetrahedral distortion, PEND = Pauling electronegativity difference and P = the polarization fraction, and all values in brackets are experimental data taken from Ref. [34] and included for comparison)

	a (Å)	c (Å)	c/a (dimensionless)	$\langle T–X–T \rangle$ (°)	δ (°)	$\langle T–X \rangle$ (Å)	$\langle T–T \rangle$ (Å)	*AT* dist (Å)	*BST* dist (Å)	*TT* dist (Å)	P (dimensionless)	PEND (dimensionless)
BeF_2	4.828559	5.282637	1.0940	147.28	13.44	1.5612	2.996	5.0E-03	2.1E−03	5.4E−03	0.61	2.41
	(4.7329)	(5.1788)	(1.0942)	(144.6)		(1.543)		(8E−3)	(2E−3)	(8E−3)		
SiO_2	4.970721	5.461784	1.0988	142.74	16.99	1.6317	3.092	1.8E−02	1.8E−03	1.8E−02	0.51	1.54
	(4.9137)	(5.4047)	(1.0999)	(143.6)		(1.609)		(2E−2)	(4E−3)	(2E−2)		
GeO_2	4.962979	5.707734	1.1490	127.07	28.74	1.7636	3.158	8.4E−02	1.8E−03	8.4E−02	0.46	1.43
	(4.9845)	(5.6477)	(1.1331)	(130.0)		(1.738)		(7E−2)	(6E−4)	(7E−2)		
CO_2	4.052290	4.600135	1.1352	132.02	24.77	1.3973	2.553	7.1E−02	1.4E−03	7.1E−02	0.27	0.89
SiS_2	5.927523	6.921014	1.1676	120.64	33.33	2.1749	3.779	1.9E−01	4.5E−03	1.9E−01	0.23	0.68
GeS_2	6.097848	7.175593	1.1767	117.00	36.18	2.2869	3.900	2.2E−01	6.4E−03	2.2E−01	0.20	0.57

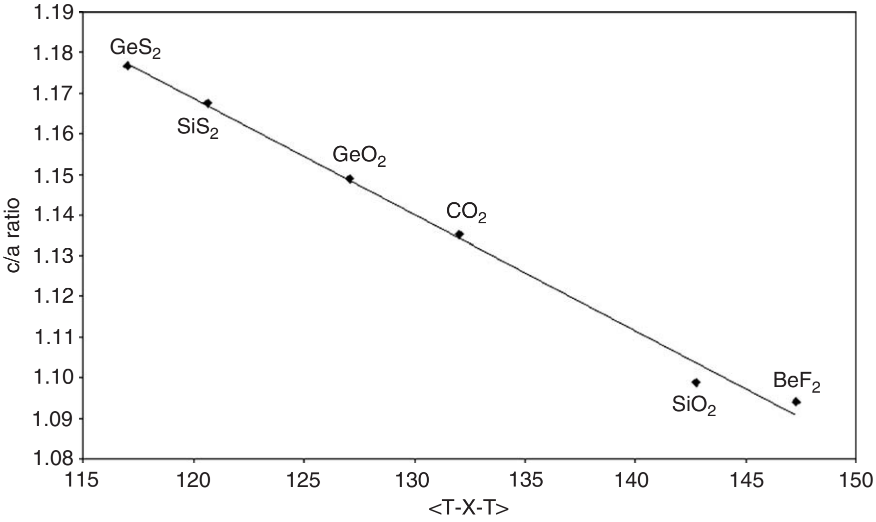

Fig. 2. c/a ratio as a function of the average T–X–T angle. The line shown is a least squares fit to the data points.

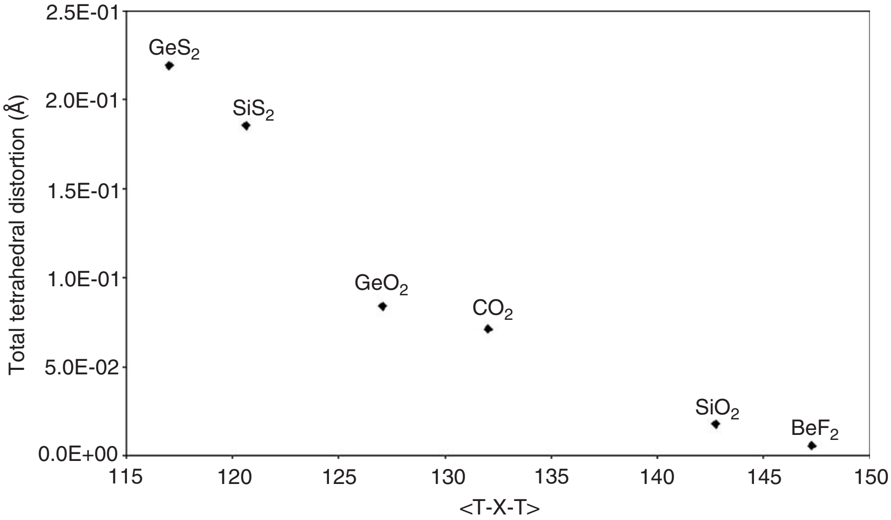

Fig. 3. Total tetrahedral distortion as a function of the average T–X–T angle.

points in our study). Both the intertetrahedral and intratetrahedral distortion in quartz thus appear to arise predominantly from the bending of T–X–T and X–T–X angles.

Philippot et al. studied the variation of the tetrahedral distortion with the average T–X–T angle, using a makeshift function defined in their paper [3]. Fig. 3 shows the change in total tetrahedral distortion with the average T–X–T angle, from our calculations. We observe that the tetrahedral distortion increases monotonically with decreasing average T–X–T angle; for the tilt angle δ we again find the same trend, but with the opposite sign (not shown). The angular tetrahedral distortion has the same trend as for the total tetrahedral distortion. For small intratetrahedral distortions this dependency of the total tetrahedral distortion on the average T–X–T angle is, as in the experimental study, approximately linear. When one also takes into account the more distorted sulphides not studied in the experiment, the relationship appears more hyperbolic in nature. This deviation away from linearity is perhaps not surprising as, with decreasing average T–X–T angle, the ratio between T–T and T–X distance decreases suggesting increased interaction between the tetrahedra. The observed correlation between both the intratetrahedral (angular and/or tetrahedral distortion) and intertetrahedral (average T–X–T angle) distortion strongly suggests that they are two sides of the same coin, linked through the topology (i.e., connectivity) of the quartz framework, in which an increase in the intertetrahedral distortion is automatically accompanied by an increase of the intratetrahedral distortion and vice versa. The precise detail of this relationship is, however, unclear as previous geometric modelling studies almost exclusively employed the simplifying condition of rigid tetrahedra.

A further observation from Table 1 is that if one increases the atomic number of the T or X atom or both (on moving down the group of the periodic table), the c/a ratio and the angular and total tetrahedral distortion increase, while the average T–X–T angle decreases. The sulphides are found to be considerably more distorted than the oxides, as are the germanium-containing structures compared to their silicon analogues. The sulphide quartz structures, in particular, have angular and total tetrahedral distortion values which in silica are only found in high energy hypothetical frameworks[2] [1], suggesting that Si and especially Ge sulphides are able to sustain larger topological strains, and thus that more highly strained frameworks might be more easily realizable as sulphides rather than as oxides. This observation is supported by the fact that the RWY framework (UCR-20 [6]), in which a tetrahedral site in a regular sodalite framework is replaced with a supertetrahedral T_4X_{10} unit possessing high topological strain, is only synthesized in the form of a sulphide or selenide and is possibly the most tetrahedrally distorted zeotype material currently known (total tetrahedral distortion >0.1 Å for UCR-20GaGeS-TAE [6]). Carbon dioxide quartz is an exception to the above rule as, even though carbon lies in the group above silicon, in terms of distortion CO_2 quartz lies in between SiO_2 and GeO_2. Finally BeF_2 quartz is found to have a smaller c/a ratio, angular and total tetrahedral distortion and a slightly larger average T–X–T angle than SiO_2 quartz. The trend between the bond stretching tetrahedral distortion and chemical composition is more erratic, but when comparing the sulphide to the non-sulphide frameworks the former consistently appear to be more distorted.

Smith's analysis formally demonstrated that, for strictly regular tetrahedra to be possible, the c/a ratio should be smaller than 1.0981; for the range of materials in Table 1 this condition is only satisfied for BeF_2. All other quartz materials must have distorted tetrahedra according to Smith's analysis, a conclusion that agrees with our calculations. The fact that we also find BeF_2 quartz to have distorted tetrahedra can be understood by the second constraint derived by Smith, i.e., that the T–X bond length should be equal to $(1/2)(\sqrt{3}a-c)$, which is 0.021 Å shorter than the actual observed value for our optimized BeF_2 structure. It is important to note here that Smith's analysis does not mean that it is mathematically impossible for strictly regular tetrahedra to exist in any of these materials (as it puts no constraints on the T–X bond length, but rather on the normalized bond length, the ratio between the bond length and the lattice constant a) merely that they cannot exist in the optimized structures. The value of the normalized bond length below which strictly regular tetrahedra are nominally possible is achieved for c/a 1.0981 (which corresponds to the idealized structure of β-quartz), at which condition the formula $(11/2)(\sqrt{3}-(c/a))$ yields a normalized bond length of $0.3170a$. In our calculation the normalized bond length of Be–F is $0.3233a$.

It appears that, even though ideal tetrahedra might thus be possible, distortions away from ideality are energetically advantageous. How can this feature be explained? Let us consider in greater detail the bonding between the central T atom and the four surrounding X atoms. Linear combination of atomic orbitals considerations suggest that each X atom is bonded to the central T atom by a single σ valence orbital completely filled with an electron pair, a picture that is supported by an analysis of the localized Wannier functions, obtained from a Boys localization of the electron density [37,38]. For each material under investigation, the Wannier functions corresponding to the T–X valence orbitals are centred along the T–X direction, and have contributions from both the T and T atoms, while the orbitals' centres of charge are seen to shift away from the middle of the bond towards the more electronegative X atom. The magnitude of this shift is defined by the polarization fraction (P) [38], which indicates how far the centre of charge projected on the bond axis for a valence electron pair (projected valence electron centre of charge, PVECC) is shifted away from the bond's midpoint ($P=0$ is the covalent limiting case with the PVECC lying exactly in the middle of the bond, while $P=1$ is the ionic limiting case with the charge centred on the most electronegative atom in the bond). Table 1 shows that the polarization fraction P decreases in the order $BeF_2>SiO_2>GeO_2>SiS_2>GeS_2$, with BeF_2 the most polarized material and GeS_2 the least polarized material in our study. Intuitively, one would assume that the polarization in the bond is a positive function of the electronegativity difference between the T and X atoms. This is verified in Fig. 4, in which we plot the polarization fraction as a function of the Pauling electronegativity difference between the T and X atoms (though we note that all electronegativity measures yield approximately the same trend). The average distance between the central T atom and the valence electron pairs $\langle$T-PVECC$\rangle$, however, is the product of the polarization fraction and the T–X bond length ($(0.5+0.5P)\langle T\text{–}X\rangle$). As the latter increases in the order $CO_2<BeF_2<SiO_2<GeO_2<SiS_2<GeS_2$, the magnitude of $\langle$T-PVECC$\rangle$ is the result of a subtle interplay between changes in atom-size and electronegativity and increases in the order $CO_2<SiO_2<BeF_2<GeO_2<SiS_2<GeS_2$.

To a first approximation, the force working against the distortion of the TX_4 tetrahedron originates from the mutual interactions between the T–X valence electron pairs described by the Wannier functions discussed above, which include electrostatic and two body short range repulsion contributions. If we neglect higher order multipoles (i.e., only consider the Coulomb contribution to the electrostatic energy) and fix the orbitals' centres of charge at a given distance away from the central T atom, as required for an

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[2] In earlier work we reported the tetrahedral mismatch (unit Å^2) rather than the RMS tetrahedral distortion, the values can be converted via: RMS tetrahedral distortion = $0.5\sqrt{(\text{tetrahedral mismatch})}$.

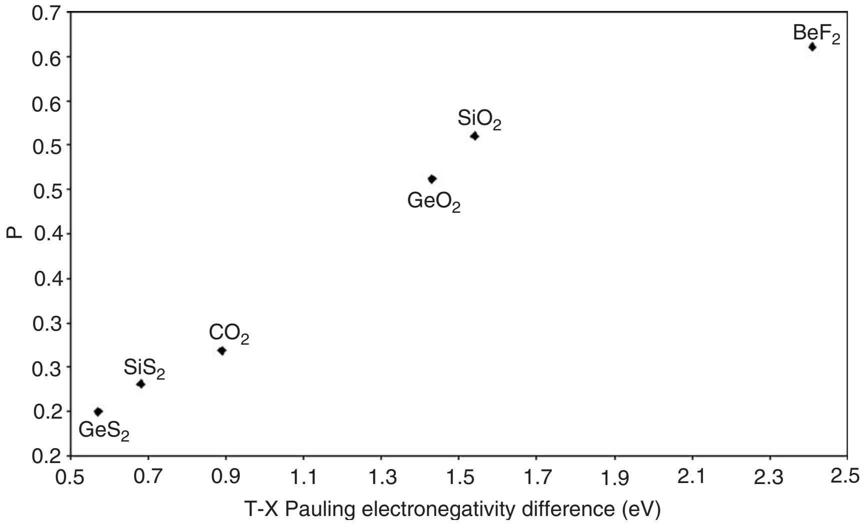

Fig. 4. Polarization fraction as a function of the Pauling electronegativity difference between the T and X atom.

ideal tetrahedron, the Coulomb energy is minimized for an angular tetrahedral distortion of zero. Deformation of a tetrahedron away from ideality (introducing angular tetrahedral distortion) thus always costs energy. As a result of the inherently asymmetric nature of the pair Coulomb potential, the energetic cost of shortening some electron pair–electron pair centre of charge distances is not compensated by the energy gained by making the other electron pair–electron pair centre of charge distances longer. Introducing a bond stretching tetrahedral distortion, i.e., allowing some T–X distances to be longer than others (and thus some electron pair centre of charges to be further away from the central T atom than others), can partly compensate for the energetic cost of the angular tetrahedral distortion, but only to a small degree as changing the T–X bond length away from its equilibrium value is also an energetically disadvantageous process. The relative strength of the Coulomb interaction, however, is inversely proportional to the distances between the electron pairs' centres of charge. Moving these centres of charge away from the central T atom, by choosing a chemical composition with increased polarization in the bond (larger T–X electronegativity difference) and/or longer T–X bonds (larger atomic radii), lowers the electrostatic contribution to the cost of distortion and makes it easier for the tetrahedron to distort. In practice, however, bond polarization and T–X bond length cannot be independently chosen (e.g., when substituting S for O the atomic radii and thus T–X bond length increases, while the electronegativity difference and thus the polarization in the bond decreases), making the effect of a substitution less clear cut. When the TX_4 tetrahedron is not isolated, but part of a crystalline lattice, it will also be subjected to a long-range electrostatic potential (the Madelung field) and to structural constraints that may break the tetrahedral symmetry. This feature can make it energetically advantageous for the tetrahedron to distort, as it may allow a bigger strain somewhere else in the crystal to be released (e.g., in the form of a relaxation of the T–X–T angles). Nonetheless, the local energetic cost of the tetrahedral distortion will still be inversely proportional to the $\langle$T-PVECC$\rangle$ distance. This simple electrostatic model rationalizes in an effective way the trend found in our calculations (and in the experimental data were available) for SiO_2, GeO_2, SiS_2 and GeS_2—as can be seen from Fig. 5 going from left to right in the above series, $\langle$T-PVECC$\rangle$ increases, indicating progressively weaker Coulomb interaction between the valence electron pairs, while the tetrahedral distortion increases monotonically in the same order. CO_2 is considerably more distorted than expected on basis of its $\langle$T-PVECC$\rangle$ distance, which is likely attributable to a non-negligible short-range repulsion of the O anions of the small CO_4 tetrahedra (the average O–O distance is 2.281 Å for CO_2 compared with 2.663 Å for SiO_2). BeF_2 on the other hand is only slightly less distorted than expected. Providing that the X–X distances are large enough to prevent the short-range repulsion of becoming significant, and ignoring the small errors due to higher order multipoles, our simple electrostatic model is thus shown to effectively explain the observed differences in tetrahedral distortion. Finally, the differences in bond stretching tetrahedral distortion possibly just reflect differences in the stiffness of the T–X bond. An important question for further work relates to whether this effect, and the observed trends in tetrahedral distortion, is unique for quartz or holds more generally for other tetrahedral framework types?

4. Conclusion

The tetrahedral distortion in a range of TX_2 quartz-like materials was studied by means of periodic DFT calculations and found to depend strongly on the chemical

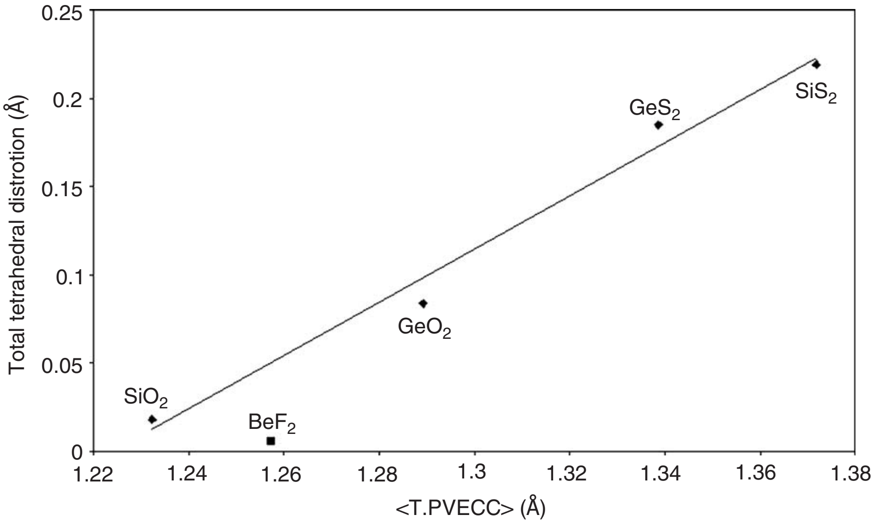

Fig. 5. Total tetrahedral distortion as a function of the ⟨T-PVECC⟩ distance (without the point for CO_2, which lies at 0.89 Å).

composition. The total tetrahedral distortion and its most sizable contribution the angular part (angular tetrahedral distortion) increases in the order of $BeF_2 < SiO_2 < CO_2 < GeO_2 < SiS_2 < GeS_2$, while the bond stretching contribution to the total tetrahedral distortion appears to vary more erratically. The sulphide materials in particular were found to have tetrahedral distortion values commonly associated in silica only with experimentally unrealizable hypothetical frameworks. None of the tetrahedra were found to be strictly regular, in line with the analysis of Smith, demonstrating that regular tetrahedra are in principle possible in quartz but that it is energetically advantageous to distort them away from ideality. A simple model is proposed that explains the ease with which tetrahedra can be distorted in terms of the relative ionicity, i.e., the charge transfer from the *T* to the *X* atom and the relative charge on the *X* (O,S,F) atom.

Acknowledgments

We kindly acknowledge Drs. A.A. Sokol and S.M. Woodley for stimulating discussion and Dr. S.A. Wells for providing us with the GASP code. M.A.Z. acknowledges the European Commission for a Marie Curie Intra-European Fellowship (MEIF-CT-2005-010326).

References

[1] M.A. Zwijnenburg, A. Simperler, S.A. Wells, R.G. Bell, J. Phys. Chem. B 109 (2005) 14783–14785.
[2] E. Philippot, A. Goiffon, A. Ibanez, M. Pintard, J. Solid State Chem. 110 (1994) 356–362.
[3] E. Philippot, D. Palmier, M. Pintard, A. Goiffon, J. Solid State Chem. 123 (1996) 1–13.
[4] C.T. Prewitt, H.S. Young, Science 149 (1965) 535–537.
[5] M.J. MacLachlan, S. Petrov, R.L. Bedard, I. Manners, G.A. Ozin, Angew. Chem. Int. Ed. 37 (1998) 2075–2079.
[6] N. Zheng, X. Bu, B. Wang, P. Feng, Science 298 (2002) 2366–2369.
[7] N. Zheng, X. Bu, P. Feng, Nature 426 (2003) 428–432.
[8] X. Bu, N. Zheng, P. Feng, Chem. Eur. J. 10 (2004) 3356–3362.
[9] W. Schnick, J. Lücke, Z. Anorg. Allg. Chem. 610 (1992) 121–126.
[10] H. Jacobs, R. Nymwegen, S. Doyle, T. Wroblewski, W. Kockelmann, Z. Anorg. Allg. Chem. 623 (1997) 1467–1474.
[11] J.M. Léger, J. Haines, L.S. de Oliveira, C. Chateau, A. Le Sauze, R. Marchand, S. Hull, J. Phys. Chem. Solids 60 (1999) 145–152.
[12] J.M. Léger, J. Haines, C. Chateau, R. Marchand, J. Phys. Chem. Solids 61 (2000) 1447–1453.
[13] J.M. Léger, J. Haines, C. Chateau, G. Bocquillon, M.W. Schmidt, S. Hull, F. Gorelli, A. Le Sauze, R. Marchand, Phys. Chem. Mineral 28 (2001) 388.
[14] S. Correll, O. Oeckler, N. Stock, W. Schnick, Angew. Chem. Int. Ed. 42 (2003) 3549–3552.
[15] A.F. Wright, A.N. Fitch, A.C. Wright, J. Solid State Chem. 73 (1988) 298–304.
[16] C.S. Yoo, H. Cynn, F. Gyci, G. Galli, V. Iota, M. Nicol, S. Carlson, D. Häusermann, C. Mailhiot, Phys. Rev. Lett. 83 (1999) 5527–5530.
[17] V. Iota, C.S. Yoo, H. Cynn, Science 283 (1999) 1510–1513.
[18] S. Serra, C. Cavazzoni, G.L. Chiarotti, S. Scandolo, E. Tosatti, Science 284 (1999) 788–790.
[19] G.S. Smith, Acta. Cryst. 16 (1963) 542–545.
[20] H. Grimm, B. Dorner, J. Phys. Chem. Solids 36 (1975) 407–413.
[21] V.R. Saunders, R. Dovesi, C. Roetti, R. Orlando, C.M. Zicovich-Wilson, N.M. Harrison, K. Doll, B. Civalleri, I.J. Bush, Ph. D'Arco, M. Llunell, CRYSTAL03 User's Manual, Universita' di Torino, Torino, 2003.
[22] A.D. Becke, J. Chem. Phys. 98 (1993) 5648–5652.
[23] http://www.crystal.unito.it/Basis_Sets/Ptable.html.
[24] C.M. Zicovich-Wilson, R. Dovesi, J. Molec. Catal. A: Chem. 119 (1997) 449–458.
[25] C.M. Zicovich-Wilson, A. Corma, J. Phys. Chem. B 104 (2000) 4134–4140.
[26] A. Lichanot, M. Chaillet, C. Larrieu, R. Dovesi, C. Pisani, Chem. Phys. 164 (1992) 383–394.
[27] M. Catti, Phys. Rev. B 65 (2002) 224115.
[28] G. Valerio, M. Catti, R. Dovesi, R. Orlando, Phys. Rev. B 52 (1995) 2422–2427.
[29] S.A. Wells, M.T. Dove, M.G. Tucker, J. Appl. Crystal. 37 (2004) 536–544.
[30] G.D. Gatta, S.A. Wells, Phys. Chem. Miner. 31 (2004) 465–474.
[31] G. Sastre, J.D. Gale, Micro. Mesop. Mater. 43 (2001) 27–40.

[32] G. Sastre, J.D. Gale, Comp. Mater. Sci. 28 (2003) 77–84.
[33] L. Levien, C.T. Prewitt, D.J. Weidner, Am. Mineral. 65 (1980) 920–930.
[34] J. Haines, O. Cambon, Z. Kristallogr. 219 (2004) 314–323.
[35] C.M. Zicovich-Wilson, F. Pascale, C. Roetti, V.R. Saunders, R. Orlando, R. Dovesi, J. Comput. Chem. 25 (2004) 1873–1881.
[36] F. Corà, M. Alfredsson, G. Mallia, D.S. Middlemiss, W.C. Mackrodt, R. Dovesi, R. Orlando, Struct. Bond. 113 (2004) 171–232.
[37] C.M. Zicovich-Wilson, R. Dovesi, V.R. Saunders, J. Chem. Phys. 115 (2001) 9708–9719.
[38] C.M. Zicovich-Wilson, A. Bert, C. Roetti, R. Dovesi, V.R. Saunders, J. Chem. Phys. 116 (2002) 1120–1127.