Electron Density and Bonding in Ring Silicates: Beryl, Cordierite, Dioptase*

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The electron density and bonding in the silicates beryl, cordierite and dioptase has been investigated. The replacement of Be, Si and Al atoms in the identical structural fragments leads to a $\delta q$-redistribution and changes the $\sigma$-bond character from slightly polar to strongly polar. The condensation of [SiO$_4$]-tetrahedra in the rings leads to the accumulation of electron density near bridge oxygens. This phenomenon is expressed especially in dioptase (pure ring silicate). Therefore, the electron density picture may be considered as a supplementary independent criterion for classification of crystal structures. The experimental $\delta q$-maps for H$_2$O molecules in dioptase are in good agreement with theoretical ones. The $\delta q$-distribution of 3d-electrons and bonding in the Jahn-Teller distorted Cu-octahedron can be interpreted from crystal-field-theory point of view.

Key words: Electron density; Bonding; Ring silicates.

The investigation of the experimental electron density distribution obtained by precise X-ray data [1] offers the possibility to analyse the chemical bonding and its peculiarities in crystals, the atomic charges, the principles of classification of crystal structures and other crystal chemical concepts on a more fundamental level. The comparison of the experimental $\delta q$-maps with theoretical ones is also very useful. A review of recent data on $\delta q$-distributions in silicates [2] shows the relevance of this approach and the insufficiency of data concerning certain groups, in particular ring silicates.

New data on orthorhombic iron-rich low-cordierite Na$_{0.04}$Al$_{2}$Si$_{3}$Fe$_{0.78}$Mn$_{0.05}$.[Al$_{2}$Si$_{6}$O$_{18}$] · 0.2 H$_2$O · 0.06 CO$_2$ and trigonal dioptase Cu$_{0.78}$Si$_{6}$O$_{18}$ · 6 H$_2$O are presented in this work. Together with hexagonal beryl Na$_{0.04}$Be$_{2.98}$Al$_{2}$Si$_{6}$O$_{18}$ · 0.3 H$_2$O [2, 3] these three minerals are classified as ring silicates [4] possessing different symmetry of the tetrahedral anionic group [T$_6$O$_{18}$]. The cations Al, (Mg, Fe, Mn) and Cu have octahedral coordination. The minor impurity of water molecules in beryl and cordierite is established within the channels. At the same time, water molecules are considered as important structural elements in dioptase, forming rings of 6 H$_2$O like [Si$_6$O$_{18}$] (Figures 1 a–c).

Table 1. Crystallographic and experimental data.

<table>
<thead>
<tr>
<th></th>
<th>Beryl</th>
<th>Cordierite</th>
<th>Dioptase</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$, Å</td>
<td>9.222 (3)</td>
<td>17.155 (5)</td>
<td>14.597 (2)</td>
</tr>
<tr>
<td>$b$, Å</td>
<td>9.222 (3)</td>
<td>9.777 (4)</td>
<td>14.597 (2)</td>
</tr>
<tr>
<td>$c$, Å</td>
<td>9.204 (1)</td>
<td>9.339 (1)</td>
<td>7.796 (14)</td>
</tr>
<tr>
<td>Sp. group</td>
<td>P6/mmc</td>
<td>C ccm</td>
<td>R3</td>
</tr>
<tr>
<td>$r_{ab}$, cm</td>
<td>0.012</td>
<td>0.0125</td>
<td>0.01</td>
</tr>
<tr>
<td>No. refl., meas.</td>
<td>4971</td>
<td>6324</td>
<td>3878</td>
</tr>
<tr>
<td>Max. no. equiv.</td>
<td>12</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>Aver. stat., $R_{int}$</td>
<td>2.3</td>
<td>2.5</td>
<td>3.5</td>
</tr>
<tr>
<td>No. indep. refl.</td>
<td>752</td>
<td>1982</td>
<td>1593</td>
</tr>
<tr>
<td>Abs. corr., $\mu$</td>
<td>0.1</td>
<td>0.33</td>
<td>0.7</td>
</tr>
<tr>
<td>Ext. corr., $R_{ext}$ (Zachariasen)</td>
<td>1566</td>
<td>6138</td>
<td>8414</td>
</tr>
<tr>
<td>Angle range for high-order refl., sin $\theta$/$\lambda$</td>
<td>0.8–1.08</td>
<td>0.65–1.08</td>
<td>0.75–1.08</td>
</tr>
<tr>
<td>No. reflection</td>
<td>338</td>
<td>1058</td>
<td>625</td>
</tr>
<tr>
<td>$R_{epl}$</td>
<td>0.7</td>
<td>1.18</td>
<td>1.90</td>
</tr>
<tr>
<td>$R_{wpl}$</td>
<td>0.79</td>
<td>1.19</td>
<td>2.00</td>
</tr>
<tr>
<td>$S$</td>
<td>1.020</td>
<td>1.023</td>
<td>0.862</td>
</tr>
</tbody>
</table>

The experimental and data-treatment conditions are given in Table 1. The models used for refinement were based on the precise determination of the cordierite structure by Armbruster [5] and by Armbruster and Bürgi [6], and of the dioptase structure by Belov et al. [7]. The results of high-order refinement were the


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Fig. 1. Crystal structures in (001)-projection:
  a) beryl,
  b) cordierite,
  c) diopside.
The unit cells and symmetry elements are shown.
The crystal structures of beryl and low-cordierite are very similar and have identical structural fragments. The reason for the lower symmetry (orthorhombic instead of hexagonal) of cordierite is considered to be the double substitution in the tetrahedra of (Mg, Fe) and (Mg, Fe) as central atoms. The latter deserves special interest owing to Jahn-Teller distortion.

Let us consider the $\delta g$-distribution of the three minerals: a) for the identical structural fragments, b) for different types of $[\text{T}_6\text{O}_{18}]$-rings, c) for $\text{H}_2\text{O}$ molecules, and d) for octahedra with Al, (Mg, Fe) and Cu as central atoms. The latter deserves special interest owing to Jahn-Teller distortion.

Fig. 2. $\delta g$-maps for identical structural fragments with 0.1 eÅ$^{-3}$ contour interval: a) Si, Be-tetrahedra, Al-octahedron, $O_1-O_1'$ common edge (beryl), b) $\text{Al}_1$, $\text{Si}_1$, $\text{M}$, $O_2-O_2'$ (cordierite), c) $\text{Al}_2$, $\text{Si}_3$, $\text{M}$, $O_3-O_4$ (cordierite).

The crystal structures of beryl and low-cordierite are very similar and have identical structural fragments. The reason for the lower symmetry (orthorhombic instead of hexagonal) of cordierite is considered to be the double substitution in the tetrahedra of the beryl crystal structure: two Si in the $[\text{T}_6\text{O}_{18}]$-ring by Al and three Be by two Al and one Si (Figures 1a, b). The replacement of the central atoms in the tetrahedra and the octahedron in the structural fragment consisting of three polyhedra leads to remarkable differences in the $\delta g$-maps for these two minerals (Figures 2a–c). The $\delta g$-maxima of 0.2 eÅ$^{-3}$ on the Be–O bond in beryl (Fig. 2a) are apparently displaced towards the oxygen atoms. Hence, Be–O $\sigma$-bonds have more polar character than the Si–O $\sigma$-bond in cordierite (Si$_1$ is situated in the Be-position), whereas the $\delta g$-peak of 0.4 eÅ$^{-3}$ (Fig. 2b) lies in the middle of the bond. The same is true for the Al$_2$–O bond (Figure 2c). In accordance with the change of the electronegativity of the elements we can also observe the $\delta g$-redistribution around the oxygen: the small maximum of 0.1 eÅ$^{-3}$ is on the (Mg, Fe)–O bond, the bigger maxima of 0.2–0.35 eÅ$^{-3}$ are on Si, Al–O bonds (Figures 2b, c). In contrast to cordierite, the $\delta g$-peaks in beryl are almost equal (0.2 eÅ$^{-3}$) between Al–O in the octahedron and Be–O in the tetrahedron with increased concentration of $\delta g$ (0.4 eÅ$^{-3}$) on Si–O bonds. It is possible to recognize on $\delta g$-maps Si–O (0.35–0.4 eÅ$^{-3}$) and Al–O (0.20–0.25 eÅ$^{-3}$) bonds in cordierite, whereas in the $[\text{Al}_2\text{Si}_4\text{O}_{18}]$-ring the $\delta g$-maxima on the bonds are “averaged”.

Three $[\text{T}_6\text{O}_{18}]$-rings with different symmetry are presented on Figures 3a–c. The puckered dioptase ring was collected from Si–O–Si’ fragments. The general rule for the $\delta g$-distribution in $[\text{T}_6\text{O}_{18}]$-units is the electron density accumulation near the bridge oxygens. The values of $\delta g$-peaks 0.3–0.4 eÅ$^{-3}$ are nearly equal in highly symmetrical beryl-rings and correlate with bond lengths (Table 2). The $\delta g$-map in cordierite has a more dispersed appearance, in agreement with the lower symmetry and the presence of both Si and Al atoms in the ring. The $\delta g$-maxima on the bridge oxygens in dioptase are much higher (0.6–0.8 eÅ$^{-3}$; the shorter Si–O bond corresponds to the largest maxima) than the ones in the first two minerals. On the other hand, comparison of the $\delta g$-maxima near bridge and nonbridge oxygens inside $[\text{T}_0\text{O}_4]$-tetrahedra in beryl and cordierite shows the absence of any significant difference (Figures 4a–c). In contrast to cordierite, in dioptase this difference is remarkable (0.2–0.3 eÅ$^{-3}$, Figure 4e). This has apparently crystal chemical reasons. According to Godovikov [10], beryl and cordierite can be classified as framework structures formed by linkage of Si$_1$, Al and Be-tetrahedra. The $[\text{Si}_3\text{O}_{18}]$-units in the dioptase crystal structure are completely isolated from each other. The redistribution of $\delta g$ inside the $[\text{SiO}_4]$-tetra-
hedra in favour of the bridge oxygen is necessary in order to maintain the puckered pure ring-silicate unit for the rigidity of the structure, though with more effort.

The H$_2$O-molecules in beryl and cordierite have the same structural position in the channel (Figures 1 a, b). They are disordered, as it follows from $\delta\rho$-maxima on O–H bonds and in accordance with the point symmetry of the O$_w$-position (622 in beryl and 222 in cordierite). Note that the planes of H$_2$O molecules are perpendicular to the c-axis in both structures.

The 6 H$_2$O-ring in dioptase is sandwiched between pairs of [Si$_6$O$_{18}$]-rings; together they form crown-shaped clusters with threefold symmetry (Figure 1 c). The experimental $\delta\rho$-maps of H$_2$O molecules in dioptase (Figs. 5 a, b) are in good agreement with theoretical ones for the free molecule [11]. The difference in $\delta\rho$-maxima on O–H bonds (0.6 eÅ$^{-3}$) and lone-pairs (0.4 eÅ$^{-3}$) can be explained if superposition effects are taken into account, which leads to an apparent decrease of the $\delta\rho$ of H$_2$O lone-pairs in the crystal. The thermal motion is the other reason of this difference in $\delta\rho$.

The $\delta\rho$-maps of the O$_w$–O$_w$ bond (Table 2) in the 6 H$_2$O-ring are in good agreement with theoretical ones [13], calculated for the same distance of about 2.6 Å.

The water-molecule rings have ice-like configuration, although the lone-pair positions are different in ice and dioptase: they are statistically disordered in the former and ordered outside the ring in the latter.
The Cu-octahedron in dioptase shows Jahn-Teller distortion (Table 2) with four equatorial oxygen atoms and two apical water molecules. The 3d energy levels of Cu$^{2+}$ in a field of tetragonal symmetry $D_{4h}$ split into four sublevels: $e_g(d_{xz}, d_{yz}), b_{2g}(d_{xy}), b_{1g}(d_{x^2-y^2}), a_{1g}(d_{z^2})$. The $\delta\rho$-maxima of 0.2–0.3 eÅ$^{-3}$ (Figs. 6a, b) on Cu–O lines near oxygens can be considered as indication of a $\sigma$-bond. The smeared $\delta\rho$-peak of 0.6 eÅ$^{-3}$ (Fig. 6b) directed towards $O_w$ is connected with the $a_{1g}$-level and partially with the $e_g$-level. Four $\delta\rho$-minima directed towards the equatorial $O$ ligands are connected with the $b_{2g}$-level, which is less occupied by electrons (Fig. 6a). Four $\delta\rho$-maxima of 0.2–0.6 eÅ$^{-3}$ in the same section are connected with the $b_{2g}$-
level. The difference in the values may be explained by the electrostatic interaction with ions from the second coordination sphere. The largest maximum of 0.6 eÅ⁻³ is observed near the O₃–O₂ edge screened outside by two silicon atoms from the [Si₆O₁₈]⁻²-ring. The main features of the δρ-distribution in the Cu Jahn-Teller octahedron in dioptase are close to that in chalciantite CuSO₄·5H₂O [14].

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