

Theoretical analysis of electronic and structural properties of anhydrous calcium oxalate

A. Koleżyński · A. Małecki

MEDICTA2009 Special Issue
© Akadémiai Kiadó, Budapest, Hungary 2009

Abstract The results of theoretical analysis of the electronic and crystal structural properties and bonding in relation to thermal decomposition process in anhydrous calcium oxalate are presented. The methods used in this analysis—topological analysis of electron density (Bader’s Quantum Theory of Atoms in Molecules approach) obtained from DFT calculations performed by Wien2k package (Full Potential Linearized Augmented Plane Wave Method); bond order model (Cioslowski&Mixon), applied to topological properties of the electron density; as well as Brown’s Bond Valence Model (bonds valences and strength’, and bond and crystal strains, calculated from crystal structure and bonds lengths data) are described. The analysis of the obtained results shows that these methods allow us to explain the way of thermal decomposition process of anhydrous calcium oxalate to calcium carbonate as a decomposition product, and to describe the structural transition taking place during such process (from monoclinic anhydrous CaC_2O_4 to rhombohedral calcite structure). In the light of the results of our similar calculations performed previously for other anhydrous oxalates (zinc, cadmium silver, cobalt, and mercury) the proposed theoretical approach can be considered as promising and reliable tool, which allow analyzing the properties of the structure and bonding and hence predicting the most probable way of thermal decomposition process for given crystal structure.

Keywords Bond order · Bond strength · Bond valence · Electron density topology · FP-LAPW DFT calculations · Thermal decomposition of oxalates

Introduction

Anhydrous metal oxalates form a group of compounds with very interesting properties, which makes them important materials for nanopowders technology (e.g., conducting precisely controlled thermal decomposition process of given oxalates to metallic or metal oxide products in a form of nanoparticles, one can obtain nanopowders possessing technologically desirable properties). Despite the fact that these compounds have very similar layered structures with monoclinic unit cells and well-defined oxalate anions surrounded by metallic cations, they decompose thermally differently to $\text{M} + \text{CO}_2$, $\text{MO} + \text{CO} + \text{CO}_2$, or $\text{MCO}_3 + \text{CO}$ [1–10].

There is still lack of consistent theoretical description and explanation of the ways of thermal decomposition paths in anhydrous oxalates, despite many experimental results available. One can however expect that the key role here plays the character and properties of chemical bonding in given oxalate, which in turn depend on the characteristic properties of metallic cation. Thus, it seems reasonable to expect that the theoretical study of fundamental features of electron density (topological analysis) and chemical bond (bond order, bond valence, bond strains etc.) should in principle lead to prediction (or at least to explanation) of metal oxalates decomposition ways.

In this article, we present the results of the theoretical analysis of electronic and crystal structural properties of anhydrous calcium oxalate and their relations with the way of thermal decomposition process (to $\text{MCO}_3 + \text{CO}$),

A. Koleżyński (✉) · A. Małecki
Faculty of Materials Science and Ceramics, AGH University
of Science and Technology, Al. Mickiewicza 30,
30-059 Kraków, Poland
e-mail: andrzej.kolezynski@agh.edu.pl

carried out by means of theoretical approach we have previously proposed and applied to silver, cadmium, cobalt, zinc, and mercury anhydrous oxalates [11–15], the theoretical analysis of the electronic properties based on the topological properties of electron density obtained from first principle calculations (Bader's Quantum Theory of Atoms in Molecules [16] formalism) together with structural consideration of bonds valence, bond strength and stresses associated with deviation of given structure from ideal one, based on the Brown's Bond Valence Method [17] founded on Pauling's "electrostatic valence rule" [18]. As our previous results suggest, such approach can give us the additional insight into the thermal decomposition process and helps not only to explain thermal decomposition path in given oxalate, but also, to some extent, to predict such most probably path for the compounds for which experimental results are unavailable.

Computational details

The electronic structure calculations for anhydrous calcium oxalate have been performed using WIEN2k FP-LAPW (Full Potential Linearized Augmented Plane Wave Method) package [19], within Density Functional Theory (DFT) formalism [20–25]. The calculations has been performed for 500 k-points ($9 \times 8 \times 6$ mesh within the irreducible Brillouin zone), cutoff parameter $Rk_{\max} = 7.5$, GGA-PBE exchange-correlation potential [26], the values of muffin-tin radii (R_i) [a.u.]: M—1.8, O—1.17, C—1.17 and the convergence criteria for SCF calculations set to $\Delta E_{\text{SCF}} \leq 10^{-5}$ Ry for total energy and $\Delta \rho_{\text{SCF}} \leq 10^{-5}$ e for electron density topology analysis. The crystal structure parameters and fractional atomic coordinates used in DFT calculations are listed in Table 1.

The calculated total SCF electron density distribution in crystal cell has been used as a basis for the calculations of the topological properties of bond critical points (within

Bader's Quantum Theory of Atoms in Molecules [16] formalism).

Crystal structure of anhydrous calcium oxalate

The crystal structure of anhydrous calcium oxalate [27] contains two types of layers which are stacked alternately along x -axis (Fig. 1—the majority of the figures have been prepared with VESTA visualization software [28]): layer1 consisting of Ca ions together with Ox1 oxalate anions, forming two alternate chains of Ca_1 and Ca_2 cations connected in (001) direction via Ox1 anions (Fig. 1, upper left), and layer2 consisting of Ox2 anions only, linking layer1 layers together (Fig. 1, upper right). The oxalate ions (Ox1 and Ox2) are in two different structural environments: Ox1 is in a planar coordination by six calcium ions (Fig. 2), and Ox2 is surrounded by four calcium ions (Fig. 3).

Results

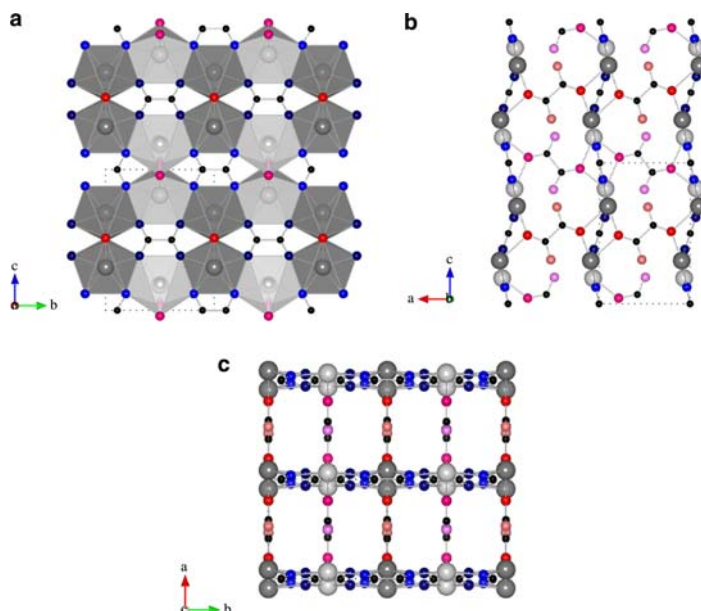
Electron density topology

The total electron density distribution data obtained from FP-LAPW SCF calculations have been used for Bader's QTAIM analysis of electron density topology. As Bader et al. [29] have shown, the analysis of the gradient vector field derived from the scalar electron density distribution provides us with the crucial information about properties of the electron density in topologically special points (so called critical points) for which gradient of the electron density $\nabla \rho(r)$ is equal to zero and thus about bonding in given molecule or crystal (detailed description of methods used in present calculations can be found in our previous articles [11–13]). The parameters characterizing bond critical points for Ca_4 and Ca_6 environment, calculated

Table 1 Anhydrous calcium oxalate crystal structure data [27]

Structure	Space group	$a/\text{Å}$	$b/\text{Å}$	$c/\text{Å}$	$\beta/^\circ$	$V/\text{Å}^3$			
CaC_2O_4	$P2/m$ (No. 10)	6.1644	7.3623	9.53720	90.242	432.83			
Fractional atomic coordinates									
Atom	x	y	z	Wyckoff position	Atom	x	y	z	Wyckoff position
Ca_1	0.0930	0.0000	0.3070	2m	O_5	0.4921	0.5000	0.1880	2n
Ca_2	0.0660	0.5000	0.1820	2n	O_6	0.7850	0.5000	0.0404	2n
O_1	0.0596	0.3120	0.3864	4o	C_1	0.0000	0.3919	0.5000	2k
O_2	0.0364	0.1880	0.1180	4o	C_2	0.0000	0.1081	0.0000	2i
O_3	0.5319	0.0000	0.3131	2m	C_3	0.4071	0.0000	0.5577	2m
O_4	0.2100	0.0000	0.5133	2m	C_4	0.5798	0.5000	0.0659	2n

Fig. 1 Anhydrous calcium oxalate crystal structure projected onto yz , xz , and xy planes



according to Bader's theory, are presented in Tables 2 and 3, respectively. Characteristic parameters of BCPs have been in turn used as a basis for the calculations of bond orders. As in our previous calculations [11–13], the bond-order formula proposed by Cioslowski and Mixon [30] (in an improved form suggested by Howard and Lamarche [31]) has been used here. The respective bond orders calculated for calcium oxalate are presented in Table 4.

Additional information about the bonding properties can be obtained from experimental crystal structure data using Bond Valence Method proposed by Brown (present state of the art and perspectives of Bond Valence Model in inorganic crystal chemistry has been reviewed by Urusov and Orlov [32] and recently by Brown [17]). This method not only gives us information about the atomic and bond valences (which can be related to bond strength and thus to bond order), but also allows us to estimate the values of the strains acting on single bonds as well as the overall strains present in given structure.

There are two different types of indicators of such stresses: d_i and D measuring, respectively, the level of deviation of given atom environment or entire crystal structure from ideal one (the magnitude of unbalanced charge for given atom in the structure or for the whole structure) and so called strain factor δ providing information about the magnitudes of and differences between the strains acting on single bonds or groups of bonds [see details in [12]]. The values of bond valences s_{ij} and bond strain factors calculated from structural data for anhydrous calcium oxalate are presented in Table 5 (we have focused here only on bond valences and bond strain factors, as ones directly related to bond properties and thus important for our analysis).

The following equations (formulated with the aid of BCPs found during the topological analysis of electron density) have been used for theoretical valences calculation in anhydrous calcium oxalate, according to Valence Sum Rule:

$$\text{Ca}_1 = r_1 + 2r_2 + 2r_3 + r_4 = \frac{2}{3} + 2 \cdot \frac{1}{4} + 2 \cdot \frac{1}{4} + \frac{1}{3} = 2$$

$$\text{Ca}_2 = r_5 + r_6 + 2r_7 + 2r_8 = \frac{2}{3} + \frac{1}{3} + 2 \cdot \frac{1}{4} + 2 \cdot \frac{1}{4} = 2$$

$$\text{O}_1 = r_3 + r_8 + r_{9a} = \frac{1}{4} + \frac{1}{4} + 1 \cdot \frac{1}{2} = 2$$

$$\text{O}_2 = r_2 + r_7 + r_{9b} = \frac{1}{4} + \frac{1}{4} + 1 \cdot \frac{1}{2} = 2$$

$$\text{O}_3 = r_{11} = 2$$

$$\text{O}_4 = r_1 + r_4 + r_{10} = \frac{2}{3} + \frac{1}{3} + 1 = 2$$

$$\text{O}_5 = r_{12} = 2$$

$$\text{O}_6 = r_5 + r_6 + r_{13} = \frac{2}{3} + \frac{1}{3} + 1 = 2$$

$$\text{C}_1 = 2r_{9a} + r_{14} = 2 \cdot 1\frac{1}{2} + 1 = 4$$

$$\text{C}_2 = 2r_{9b} + r_{14} = 2 \cdot 1\frac{1}{2} + 1 = 4$$

$$\text{C}_3 = r_{10} + r_{11} + r_{15a} = 1 + 2 + 1 = 4$$

$$\text{C}_4 = r_{12} + r_{13} + r_{15b} = 2 + 1 + 1 = 4$$

Discussion

Since Ca_4 and Ca_6 environments of oxalate anions are very different, it is reasonable to analyze them separately. We begin our analysis for the Ca_4 environment, where in our opinion decomposition process starts. The results presented

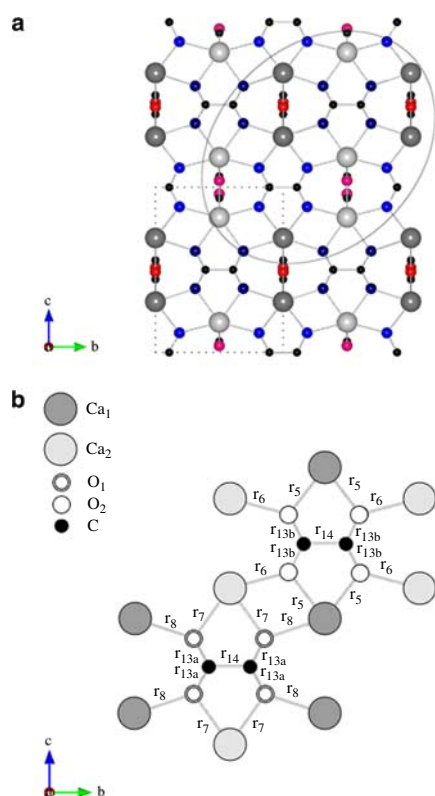


Fig. 2 Ox1 oxalate anion Ca_6 environment. Respective bond lengths are presented in Table 2

in Table 4 show that the weakest bonds here are those created between carbon atoms within oxalate groups (r_{15a} and r_{15b}), slightly stronger are Ca–O bonds (r_1 – r_4), and the strongest ones are C–O bonds (r_9 – r_{12}) and in addition r_9 and r_{11} are slightly stronger than r_{10} and r_{12} . From Table 2, we can draw the conclusions that Ca–O bonds are ionic-covalent with strong ionic component of bond character, while C–O and C–C bonds are covalent (with quite high values of ellipticity and higher localization of electron density in BCP region for C–O bonds). These results allow us to propose the most probable order of bond breaking in Ca_4 environment during thermal decomposition process (see Fig. 4) first, the C–C bonds (r_{15a} and r_{15b}) break. This will result in charge flow to remaining C–O bonds (presumably to a higher extent to r_{10} and r_{12} bonds, since the oxygen atoms O_3 and O_5 are connected only to carbon atoms via these bonds) and their strengthening. Next, the r_9 and the r_{11} bonds break and CO molecules are set free and the layer layer1, along x direction, are being separated and at the same time oxygen atoms O_4 and O_6 remain bonded to respective calcium atoms. These conclusions are confirmed by the results of BVM calculations. The internal strains calculated for calcium oxalate structure (Table 5) show that in comparison to the ideal relaxed structure, the C–C bonds are stretched, which—taking into account the

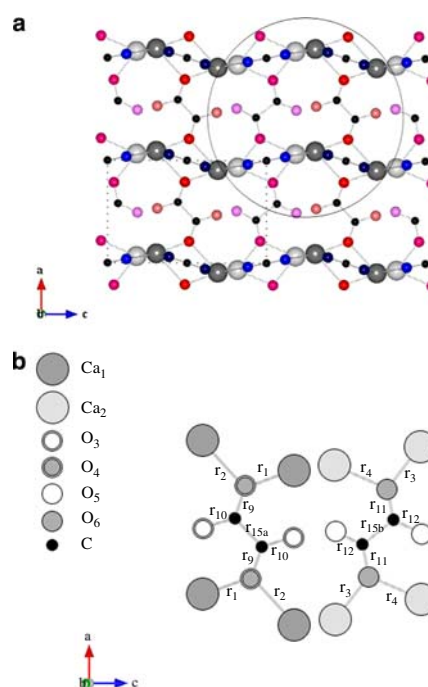


Fig. 3 Ox2 oxalate anion Ca_4 environment. Respective bond lengths are presented in Table 3

fact of their relative weakness—will promote their breaking; Ca–O bonds (r_1 – r_3) are stretched and will tend to shorten after C–C bonds break, while r_4 bond will only slightly increase its length; two C–O bonds (r_9 and r_{11}) are too short and thus should lengthen, while the other two (r_{10} and r_{12}) are too long and should decrease their lengths.

The case of Ca_6 environment is slightly different. Here, we have more symmetrical bonds (Table 4) as in previous case the weakest are C–C bonds (r_{14}), the Ca–O bonds (r_5 – r_8) are little bit stronger, and the strongest are C–O bonds (r_{13a} and r_{13b}). From the results of the topological properties of electron density calculations (Table 3) follow that again Ca–O bonds are ionic-covalent with strong ionic component of bond character, while C–O and C–C bonds are covalent (similarly as in Ca_4 case with noticeable high values of ellipticity and at the same time higher localization of electron density in BCP region for C–O, than for C–C bonds). According to these data, we propose the following sequence of consecutive steps during the thermal decomposition process (see Fig. 5): first, the C–C bond breaks as the weakest one (Fig. 5a). This allows both carbon atoms connected to neighboring oxygen atoms to rotate freely around the axis connecting respective oxygen atoms in COO group. Since as a result of bond breaking in Ca_4 environment, O_4 and O_6 oxygen atoms have remained bounded to neighboring calcium atoms, they also can freely rotate around the virtual axis connecting these calcium atoms. Due to these rotational (and simultaneously translational) vibrations of carbon and oxygen atoms, the

Table 2 Bond lengths R_{AB} , Hessian eigenvalues λ_1 – λ_3 , electron density ρ_{BCP} , Laplacian $\nabla^2\rho(r)$, and ellipticity in BCP, calculated for anhydrous calcium oxalate (Ca₄ oxalate environment)

CaC ₂ O ₄	$R_{AB}/\text{Å}$	$\lambda_1/\text{Å}^{-5}$	$\lambda_2/\text{Å}^{-5}$	$\lambda_3/\text{Å}^{-5}$	$\rho_{BCP}/e/\text{Å}^3$	$\nabla^2\rho(r)/\text{Å}^{-5}$	ϵ
r ₁ (Ca ₁ –O _{4a})	2.09268	–2.77382	–2.69430	13.51006	0.49770	8.04194	0.030
r ₂ (Ca ₁ –O _{4b})	2.54028	–0.69912	–0.69478	4.04868	0.16640	2.65478	0.006
r ₃ (Ca ₂ –O _{6a})	2.19192	–1.98722	–1.97710	10.27111	0.38610	6.30679	0.005
r ₄ (Ca ₂ –O _{6b})	2.31495	–1.41776	–1.37799	7.47077	0.28880	4.67502	0.029
r ₉ (C ₃ –O ₄)	1.28499	–21.28208	–19.57826	24.34028	2.42060	–16.52006	0.087
r ₁₀ (C ₃ –O ₃)	1.28678	–21.41221	–19.16857	21.52307	2.45030	–19.05771	0.117
r ₁₁ (C ₄ –O ₆)	1.28912	–20.81455	–19.28666	23.98361	2.38690	–16.11760	0.079
r ₁₂ (C ₄ –O ₅)	1.28593	–21.51343	–19.15893	21.31341	2.46040	–19.35895	0.123
r _{15a} (C ₃ –C ₃)	1.59178	–11.30979	–10.03494	9.72888	1.53730	–11.61585	0.127
r _{15b} (C ₄ –C ₄)	1.59297	–11.29774	–10.00361	9.73611	1.53390	–11.56524	0.129

Table 3 Bond lengths R_{AB} , Hessian eigenvalues λ_1 – λ_3 , electron density ρ_{BCP} , Laplacian $\nabla^2\rho(r)$, and ellipticity in BCP, calculated for anhydrous calcium oxalate (Ca₆ oxalate environment)

CaC ₂ O ₄	$R_{AB}/\text{Å}$	$\lambda_1/\text{Å}^{-5}$	$\lambda_2/\text{Å}^{-5}$	$\lambda_3/\text{Å}^{-5}$	$\rho_{BCP}/e/\text{Å}^3$	$\nabla^2\rho(r)/\text{Å}^{-5}$	ϵ
r ₅ (Ca ₁ –O ₂)	2.29810	–1.50524	–1.45848	7.93589	0.30540	4.97217	0.032
r ₆ (Ca ₂ –O ₂)	2.38355	–1.11025	–1.09724	6.17423	0.23430	3.96674	0.012
r ₇ (Ca ₂ –O ₁)	2.39126	–1.13170	–1.10326	6.14531	0.24500	3.91035	0.026
r ₈ (Ca ₁ –O ₁)	2.42766	–0.95457	–0.94083	5.46089	0.20880	3.56549	0.015
r _{13a} (C ₁ –O ₁)	1.28770	–21.17845	–19.27702	22.75454	2.42060	–17.70093	0.099
r _{13b} (C ₂ –O ₂)	1.28870	–21.13989	–19.24569	22.39064	2.41930	–17.99494	0.098
r ₁₄ (C ₁ –C ₁ ; C ₂ –C ₂)	1.59173	–11.35317	–10.07350	9.73129	1.54000	–11.69538	0.127

respective carbon and oxygen atoms approach to each other (the shortest C–O distance is about 1.23 and 1.3 Å for C–O₆ and C–O₄ pairs, respectively) and new C–O bonds are created (Fig. 5e). As a result, the CO₃ functional group is formed (we can treat it as a well-defined functional group since C–O bonds are strongly covalent, while remaining Ca–O bonds are strongly ionic, with small component of covalent character). Once again, above conclusions are confirmed by the results of BVM calculations: the results presented in Table 5 indicate that C–C bonds are stretched, which similarly as in case of Ca₄ environment will promote their breaking; the Ca–O bonds (r₅–r₈) are pressed and will tend to lengthen, while C–O bonds are slightly stretched and should shorten a little.

To Sum up, as a result of the proposed sequence of consecutive steps of bond breaking/creating during the thermal decomposition process, we obtain the structure of loosely connected set of layers of Ca atoms with CO₃ groups located between them and removed CO molecules; an intermediate structure in the process of calcite structure formation as a product of decomposition process.

Two questions arise here: first, is the process of structure transformation from intermediate structure described above to calcium carbonate rhombohedral one likely to occur; and

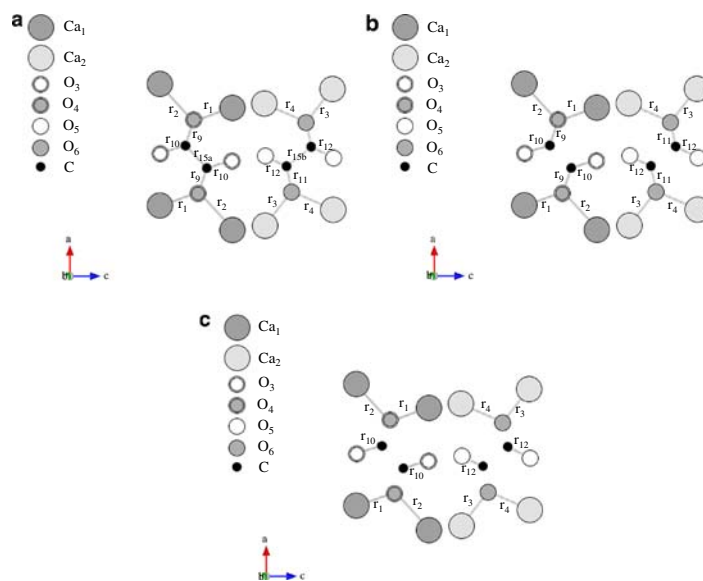
Table 4 Bond orders calculated from topological properties of electron density in bond critical points for anhydrous calcium oxalate for Ca₆ and Ca₄ anion environments (2nd and 4th column, respectively)

Bond no.	$n_{CM(HL)}$	Bond no.	$n_{CM(HL)}$
r ₅ (Ca ₁ –O ₂)	0.86	r ₁ (Ca ₁ –O _{4a})	0.93
r ₆ (Ca ₂ –O ₂)	0.84	r ₂ (Ca ₁ –O _{4b})	0.82
r ₇ (Ca ₂ –O ₁)	0.84	r ₃ (Ca ₂ –O _{6a})	0.89
r ₈ (Ca ₁ –O ₁)	0.84	r ₄ (Ca ₂ –O _{6b})	0.86
r _{13a} (C ₁ –O ₁)	1.03	r ₉ (C ₃ –O ₄)	1.05
r _{13b} (C ₂ –O ₂)	1.02	r ₁₀ (C ₃ –O ₃)	1.01
r ₁₄ (C ₁ –C ₁ ; C ₂ –C ₂)	0.73	r ₁₁ (C ₄ –O ₆)	1.04
		r ₁₂ (C ₄ –O ₅)	1.01
		r _{15a} (C ₃ –C ₃)	0.72
		r _{15b} (C ₄ –C ₄)	0.72

the second, even more important, how one can obtain the calcite structure from such intermediate structure? Our answer for the first question is positive, since according to the data from Table 5, the oxalate structure strongly deviates from ideal one and is a subject of high strains. Hence, after first bonds break this structure will surely transform to minimize the strains. For the second one on

Table 5 Theoretical and experimental bond lengths and valences and bond strain factors calculated for anhydrous calcium oxalates (see details in text)

CaC ₂ O ₄	R_{theor}	R_{exp}	s_{ij}^{theor}		δ			
r_1 (Ca ₁ –O _{4a})	2.0622	2.0927	$\frac{2}{3}$	0.6190	$\delta_{\text{Ca-O}}$	0.0955	$\delta_{\text{Ca}_1\text{-O}_{4a}}$	0.0477
r_2 (Ca ₁ –O _{4b})	2.3464	2.5403	$\frac{1}{3}$	0.2078			$\delta_{\text{Ca}_1\text{-O}_{4b}}$	0.1256
r_3 (Ca ₂ –O _{6a})	2.0622	2.1919	$\frac{2}{3}$	0.4859			$\delta_{\text{Ca}_2\text{-O}_{6a}}$	0.1808
r_4 (Ca ₂ –O _{6b})	2.3464	2.3150	$\frac{1}{3}$	0.3599			$\delta_{\text{Ca}_2\text{-O}_{6b}}$	0.0266
r_5 (Ca ₁ –O ₂)	2.4644	2.2981	$\frac{1}{4}$	0.3750			$\delta_{\text{Ca}_1\text{-O}_{2a}}$	0.1250
r_6 (Ca ₂ –O ₂)	2.4644	2.3836	$\frac{1}{4}$	0.3045			$\delta_{\text{Ca}_2\text{-O}_2}$	0.0545
r_7 (Ca ₂ –O ₁)	2.4644	2.3913	$\frac{1}{4}$	0.2988			$\delta_{\text{Ca}_2\text{-O}_1}$	0.0488
r_8 (Ca ₁ –O ₁)	2.4644	2.4277	$\frac{1}{4}$	0.2734			$\delta_{\text{Ca}_1\text{-O}_1}$	0.0234
r_9 (C ₃ –O ₄)	1.3900	1.2850	1	1.3282	$\delta_{\text{C-O}}$	0.4452	$\delta_{\text{C}_3\text{-O}_4}$	0.3282
r_{10} (C ₃ –O ₃)	1.1335	1.2868	2	1.3218			$\delta_{\text{C}_3\text{-O}_3}$	0.6782
r_{11} (C ₄ –O ₆)	1.3900	1.2891	1	1.3134			$\delta_{\text{C}_4\text{-O}_6}$	0.3134
r_{12} (C ₄ –O ₅)	1.1335	1.2859	2	1.3248			$\delta_{\text{C}_4\text{-O}_5}$	0.6752
r_{13a} (C ₁ –O ₁)	1.2400	1.2877	$\frac{1}{2}$	1.3185			$\delta_{\text{C}_1\text{-O}_1}$	0.1815
r_{13b} (C ₂ –O ₂)	1.2400	1.2887	$\frac{1}{2}$	1.3149			$\delta_{\text{C}_2\text{-O}_2}$	0.1851
r_{14} (C ₁ –C ₁ ; C ₂ –C ₂)	1.5400	1.5917	1	0.8695	$\delta_{\text{C-C}}$	0.1312	$\delta_{\text{C}_1\text{-O}_1;\text{C}_2\text{-O}_2}$	0.1305
r_{15a} (C ₃ –C ₃)	1.5400	1.5918	1	0.8694	δ_{Struct}	0.2719	$\delta_{\text{C}_3\text{-C}_3}$	0.1306
r_{15b} (C ₄ –C ₄)	1.5400	1.5930	1	0.8666			$\delta_{\text{C}_4\text{-C}_4}$	0.1334

Fig. 4 Bond breaking sequence in anhydrous calcium oxalate—Ca₄ environment

how such reconfiguration and structure transition goes, our proposition is as follows. Calcite (Fig. 6) has a rhombohedral crystal structure R-3 c (SG no. 167) with CO₃ groups surrounded by six calcium atoms (every CO₃ group is located within deformed Ca octahedron). The C–O bonds are mostly covalent, while Ca–O bonds are mostly ionic. So this structure seems to be very similar to the intermediate structure obtained during thermal decomposition process. Since this similarity can be apparent, let us take a closer look at the both the structures.

The detailed comparison of the positions and interatomic distances in the intermediate structures and in calcite crystal for both Ca environments in original oxalate structure with respective parts of calcite structure are presented in Figs. 7 and 8. In case of Ca₄ environment (Fig. 7a), we can see that the structure is strongly deformed and since there are now no bonds between layers (no oxalate anions here) the structure will exhibit the tendency to shorten the distance between layers (after removing CO molecules, vertically); to lengthen the respective distances (horizontally, due to the

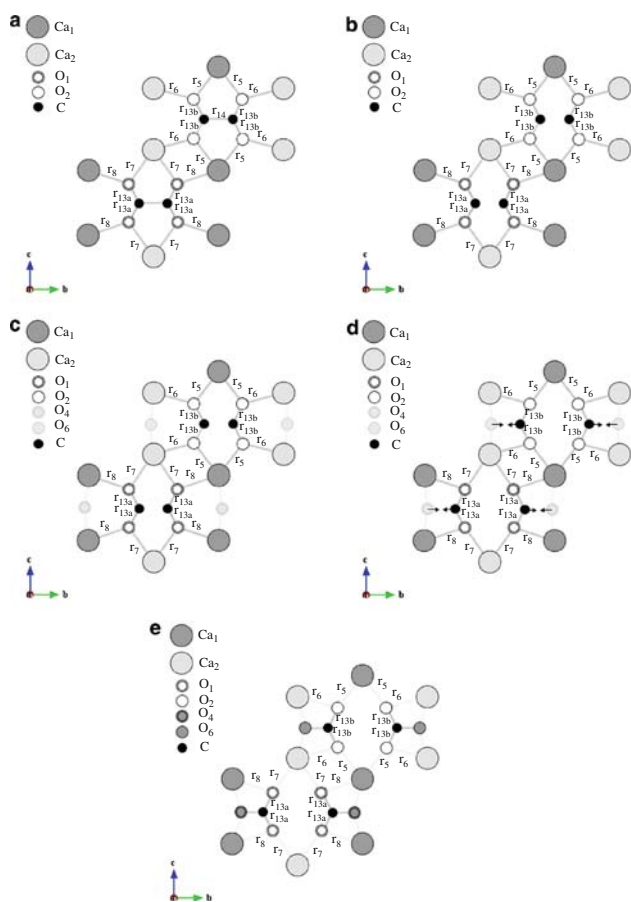


Fig. 5 Bond breaking and forming sequences in anhydrous calcium oxalate—Ca₆ environment

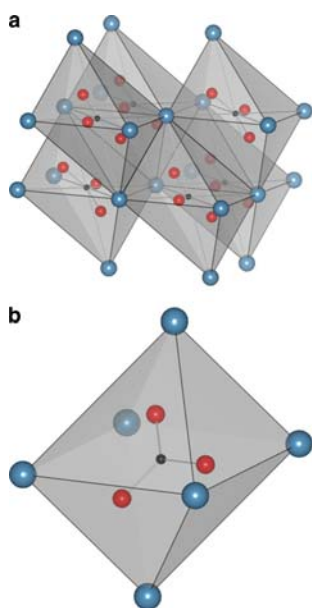


Fig. 6 Calcite crystal structure (a) and single octahedron surrounding CO₃²⁻ anion (b)

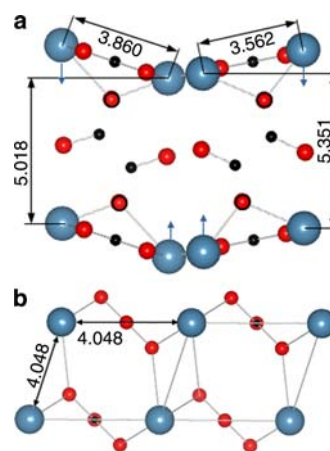


Fig. 7 Crystal structure transition from a calcium oxalate to b calcium carbonate (Ca₄ oxalate environment; the proximity of two pairs of calcium atoms is apparent here due to projection along y-axis)

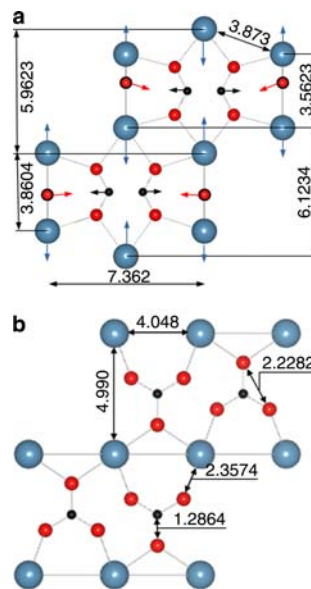


Fig. 8 Crystal structure transition from a calcium oxalate to b calcium carbonate (Ca₆ oxalate environment)

formation of CO₃ groups) and to necessary rotations and translations of whole CO₃ groups to minimize the electrostatic forces within the structure at the same time (this should be relatively easy due to the mostly ionic interactions between calcium and oxygen atoms).

The necessary structural changes during electrostatic forces minimization for Ca₆ environment is presented at Fig. 8. The arrows indicate the direction of necessary translations for respective atoms. As is clearly visible, and what the similarity of both structures suggests, such structure transformation is very likely, and as a result the product of thermal decomposition process will be calcite structure—in agreement with the experimental data.

Summary

The main purpose of this article is the application of previously proposed theoretical approach based on electron density topology and structural data to the description and explanation of the structure and bonding properties of anhydrous calcium oxalate and their relations with thermal decomposition process, which in this case leads to calcite and carbon oxide as products. Presented results allow us to propose the most probable sequence of bond breaking during the thermal decomposition process and to explain how the transition from anhydrous oxalate structure to calcite one goes. The way of thermal decomposition is in this case different than in case of *d*-electron metals oxalates [11–15]. In our opinion, this important difference in the behavior and ways of thermal decomposition process of calcium (and also of the other alkaline and alkaline earth metals [33]) and *d*-electron metals oxalates is caused by the nature of chemical bonds between metal and oxygen atoms—in former case these bonds are strongly ionic, giving the oxalate groups some freedom to change their orientation and position, and thus allowing respective carbonate structures to be formed; while in latter case the Me–O bonds are directional with much more covalent character, making such movements of the oxalate group very difficult, and thus the formation of carbonate very unlikely.

Acknowledgement This work has been supported by AGH-UST Grant no 11.11.160.110.

References

- Małecka B, Drożdż-Cieśla E, Małecki A. Mechanism and kinetics of thermal decomposition of zinc oxalate. *Thermochim Acta*. 2004;423:13–8.
- Brown ME, Dollimore D, Galwey AK. Comprehensive chemical kinetics. In: Bamford CH, Tipper CFH, editors. *Reactions in solid state*, vol. 2. Amsterdam: Elsevier; 1980.
- Boldyrev VV, Nevyantsev IS, Mikhailov YI, Khayretdinov EF. K voprosu o myekhanizmye tyermichyeskogo razlozheniya oksalatov. *Kinet Katal*. 1970;11:367–73.
- Borchardt HJ, Daniels F. The application of differential thermal analysis to the study of reaction kinetics. *J Am Chem Soc*. 1957;79:41–6.
- Dollimore D. The thermal decomposition of oxalates. A review. *Thermochim Acta*. 1987;117:331–63.
- Randhawa BS, Kaur M. A comparative study on the thermal decomposition of some transition metal maleates and fumarates. *J Therm Anal Calorim*. 2007;89(1):251–5.
- Galwey AK, Brown ME. An appreciation of the chemical approach of V. V. Boldyrev to the study of the decomposition of solids. *J Therm Anal Calorim*. 2007;90(1):9–22.
- Fujita J, Nakamoto K, Kobayashi M. Infrared spectra of metallic complexes. III. The infrared spectra of metallic oxalates. *J Phys Chem*. 1957;61(7):1014–5.
- Rane S, Uskaikar H, Pednekar R, Mhalsikar R. The low temperature synthesis of metal oxides by novel hydrazine method. *J Therm Anal Calorim*. 2007;90(3):627–38.
- Bîrzescu M, Niculescu M, Dumitru R, Carp O, Segal E. Synthesis, structural characterization and thermal analysis of the cobalt(II) oxalate obtained through the reaction of 1,2-ethanediol with $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. *J Therm Anal Calorim*. 2009;96(3): 979–86.
- Koleżyński A, Małecki A. Theoretical studies of thermal decomposition of anhydrous cadmium and silver oxalates. Part I: Electronic structure calculations. *J Therm Anal Calorim*. 2009; 96(1):161–5.
- Koleżyński A, Małecki A. Theoretical studies of thermal decomposition of anhydrous cadmium and silver oxalates. Part II: Correlations between the electronic structure and the ways of thermal decomposition. *J Therm Anal Calorim*. 2009;96(1): 167–73.
- Koleżyński A, Małecki A. First principles studies of thermal decomposition of anhydrous zinc oxalate. *J Therm Anal Calorim*. 2009;96(2):645–51.
- Koleżyński A, Małecki A. Theoretical approach to thermal decomposition process of chosen anhydrous oxalates. *J Therm Anal Calorim*. 2009;97(1):77–83.
- Koleżyński A, Małecki A. Theoretical studies of electronic and crystal structure properties of anhydrous mercury oxalate. *J Therm Anal Calorim*. (under review).
- Bader RFW. *Atoms in molecules: a quantum theory*. Oxford: Clarendon Press; 1990.
- Brown ID. *The chemical bond in inorganic chemistry: the bond valence model*. Oxford: Oxford University Press; 2002.
- Pauling L. The principles determining the structure of complex ionic crystals. *J Am Chem Soc*. 1929;51:1010–26.
- Błaha P, Schwarz K, Madsen GKH, Kvasnicka D, J. Luitz. WIEN2k, an augmented plane wave + local orbitals program for calculating crystal properties. Wien: Karlheinz Schwarz, Techn. Universität Wien; 2001. ISBN: 3-9501031-1-2.
- Slater JC. Wave functions in a periodic potential. *Phys Rev*. 1937;51:846–51.
- Loucks TL. *Augmented plane wave method*. New York: Benjamin; 1967.
- Andersen OK. Simple approach to the band-structure problem. *Solid State Commun*. 1973;13(2):133–6.
- Hamann DR. Semiconductor charge densities with hard-core and soft-core pseudopotentials. *Phys Rev Lett*. 1979;42(10):662–5.
- Wimmer E, Krakauer H, Weinert M, Freeman AJ. Full-potential self-consistent linearized-augmented-plane-wave method for calculating the electronic structure of molecules and surfaces: O_2 molecule. *Phys Rev B*. 1981;24(2):864–75.
- Singh DJ. *Planewaves, pseudopotentials and the LAPW method*. Dordrecht: Kluwer Academic Publishers; 1994.
- Perdew JP, Burke K, Ernzerhof M. Generalized gradient approximation made simple. *Phys Rev Lett*. 1996;77:3865–8.
- Hochrein O, Annu T, Kniep R. Revealing the crystal structure of anhydrous calcium oxalate, $\text{Ca}[\text{C}_2\text{O}_4]$, by a combination of atomistic simulation and Rietveld refinement. *Z Anorg Allg Chem*. 2008;634(11):1826–9.
- Momma K, Izumi F. VESTA: a three-dimensional visualization system for electronic and structural analysis. *J Appl Crystallogr*. 2008;41(3):653–8.
- Bader RFW, Slee TS, Cremer D, Kraka E. Description of conjugation and hyperconjugation in terms of electron distributions. *J Am Chem Soc*. 1983;105(15):5061–8.
- Cioslowski J, Mixon ST. Covalent bond orders in the topological theory of atoms in molecules. *J Am Chem Soc*. 1991;113(11): 4142–5.

31. Howard ST, Lamarche O. Description of covalent bond orders using the charge density topology. *J Phys Org Chem*. 2003;16(2): 133–41.
32. Urusov VS, Orlov IP. State-of-art and perspectives of the bond-valence model in inorganic crystal chemistry. *Crystallogr Rep*. 1999;44(4):686–709.
33. Koleżyński A. Crystal structure, electronic structure and bonding properties of anhydrous metal oxalates. Habilitation monograph (in polish). In preparation. To be published in: *Ceramics*. Krakow: Papers of the Commission on Ceramic Science of Polish Academy of Sciences; 2010.