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Thermal Expansion Studies of $CaO \cdot 2Al_2O_3$. A New Refractory Material

by G. Wójcik[*] and I. Mossakowska

Institute of Physical & Theoretical Chemistry, Wrocław University of Technology,
Wyb. Wyspiańskiego 27, 50-370 Wrocław, Poland
E-mail: wojcik@kchf.ch.pwr.wroc.pl

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The X-ray diffraction measurements of a $CaAl_4O_7$ single crystal have been performed at seven temperatures above ambient, over a 300–773 K temperature range. The evolution of the lattice parameters was used to determine the second rank thermal expansion tensor of the crystal. The thermal expansion is minor and highly anisotropic. The principal thermal expansion coefficients are: $7.91 \cdot 10^{-6}$, $1.12 \cdot 10^{-5}$ and $-3.48 \cdot 10^{-6}$ deg^{-1}. The results are discussed in relation to the crystal structure.

Key words: thermal expansion tensor, multi-temperature crystal structure, calcium dialuminate, refractory material

Calcium dialuminate $CaAl_4O_7$ (also written in an equivalent oxide notation as $CaO \cdot 2Al_2O_3$) is known to be used as a component of refractory cements. Recently this compound drew attention of material engineers due to its extremely low thermal expansion and resulting potential application as refractory ceramics. The compound combined in various proportions with another refractory material, $MgAl_2O_4$, exhibits extremely low thermal expansion up to 900°C [1]. This is a relevant factor for refractory ceramics ensuring an excellent resistance to thermal shocks. The newly reported refractory materials based on $CaAl_4O_7$, *e.g.* compositions with granular fractures of $MgAl_2O_4$ and $CaZrO_3$ show effects of further lowering the expansion [2]. The investigation of thermal expansion of a pure $CaAl_4O_7$ crystal at high temperatures have been undertaken in order to explore the thermal behaviour of the material.

EXPERIMENTAL

Crystals of $CaAl_4O_7$ have been grown from the melt. The X-ray diffraction measurements of a single crystal specimen were performed on a *KM4CCD* automatic diffractometer produced by KUMA Diffraction and equipped with an area detector and a heating unit. The experiment was carried out at several temperatures: 300 K, 340 K, 375 K, 473 K, 573 K, 673 K and 773 K. The precision of the temperature stability was equal to 1 degree. The tip of the thermal lag was placed at the distance of 6 mm from the sample. MoKα radiation ($\lambda = 0.71073$ Å) was used. During the data collection ω scans were performed. No absorption corrections were used. Data reductions were performed with KUMA *KM4CCD* software [3]. The

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[*] Author for correspondence.

structures were solved by direct methods [4] and refined by least-squares with the programs from the *SHELXL97* package [5]. Atomic scattering factors were taken from the *International Tables for Crystallography* [6]. The details of the data collection and the refinement at ambient are collected in Table 1.

Table 1. Experimental and refinement details at room temperature.

Crystal data	
Chemical formula	$CaO\cdot 2Al_2O_3$
Chemical formula weight	259.89
Space group	*C2/c*
a (Å)	12.857 (3)
b (Å)	8.853 (2)
c (Å)	5.435 (1)
β (°)	106.75(3)
V (Å^3)	592.4(2)
Z	4
D_x (Mg m^{-3})	2.915
No of reflections for cell parameters	474
θ range (°)	28.3
μ (mm^{-1})	1.643
Crystal size (mm)	0.87×0.59×0.56
Data collection	
No of measured reflections	1590
No of independent reflections	1101
No of observed reflections	694
Criterion for observed reflections	$I>2\sigma(I)$
$\theta_{\max}$ (°)	28.57
R_{int}	0.0323
Range of h, k, l	$-16 \leq h \leq 16$
	$-8 \leq k \leq 11$
	$-6 \leq l \leq 7$
Refinement	
$R\ [F^2 > 2\sigma(F^2)]$	0.0254
$wR\,(F^2)$	0.0749
Goodness-of-fit	1.141
No of reflections used in refinement	1101
No of parameters used	109
$\Delta\rho_{\max}$ (e/Å^3)	0.56
$\Delta\rho_{\min}$ (e/Å^3)	–0.59

The crystal structure of $CaAl_4O_7$ have been determined in 1970 [7,8]. Our results corroborate the previous ones. The structure is determined in the centrosymmetric *C2/c* space group. The reliability index R_1 is equal to about 0.025 that is a far better result than reported in [7].

RESULTS AND DISCUSSION

The crystal structure is stable over the whole temperature range covered by the experiment and does not show any phase transition. This is the monoclinic structure first mentioned in [9]. No signs of another orthorhombic polymorph, also mentioned in [9], have been observed. Table 2 reports the lattice parameters determined at seven temperatures between ambient and 773 K. The thermal evolution of the lattice parameters' relative increase is shown in Fig. 1. The thermal expansion of the crystal influences only slightly the *c* parameter value.

Table 2. The lattice parameters determined at variable temperatures.

Temperature [K]	a [Å]	b [Å]	c [Å]	β [deg]
300	12.859	8.853	5.434	106.77
340	12.869	8.859	5.437	106.88
375	12.875	8.850	5.435	106.90
473	12.876	8.875	5.434	107.08
573	12.892	8.887	5.439	107.13
673	12.892	8.885	5.435	107.16
773	12.905	8.898	5.437	107.26

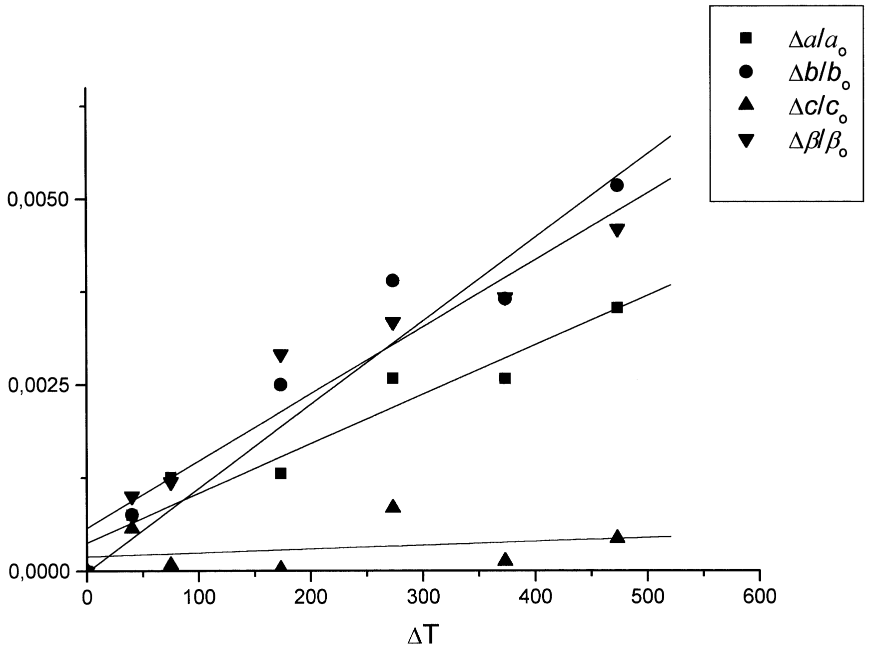

Figure 1. The lattice parameters' relative increase as a function of temperature. The lines are the linear fits to the experimental points.

The relative increase of the parameters has been fitted by linear functions. The bulk thermal expansion coefficient defined as:

$$\alpha_v = \frac{1}{V_o}\cdot\frac{dV}{dT}$$

(where V_0 denotes the unit cell volume at 300 K) equals to $1.5 \cdot 10^{-5}$ deg^{-1}, which is a small value. The thermal expansion tensor in the orthogonal coordinate system has been calculated according to the algorithms given for example by Cole *et al*. [10] and assuming the thermal expansion independence on temperature:

$$\alpha_{11} = \frac{1}{a_0} \cdot \frac{da}{dT} + \mathrm{ctg}(\beta) \cdot \frac{d\beta}{dT}$$

$$\alpha_{22} = \frac{1}{b_0} \cdot \frac{db}{dT}$$

$$\alpha_{33} = \frac{1}{c_0} \cdot \frac{dc}{dT}$$

$$\alpha_{13} = \alpha_{31} = \frac{1}{2}\left[\mathrm{ctg}(\beta)\left(\frac{1}{a_0} \cdot \frac{da}{dT} - \frac{1}{c_0} \cdot \frac{dc}{dT}\right) - \frac{d\beta}{dT}\right]$$

where a_0, b_0 and c_0 correspond to the unit cell parameters at 300 K.

The thermal expansion tensor in the orthogonal system of crystallographic axes (a^*, b, c) is:

$$\begin{bmatrix} (3.92 \pm 1.08) \cdot 10^{-6} & 0 & (-5.43 \pm 1.5) \cdot 10^{-6} \\ 0 & (1.12 \pm 0.17) \cdot 10^{-5} & 0 \\ (-5.43 \pm 1.5) \cdot 10^{-6} & 0 & (5.09 \pm 7.8) \cdot 10^{-7} \end{bmatrix}$$

After diagonalisation of the matrix we obtained the eigenvalues of the thermal expansion tensor. These are the principal thermal expansion coefficients equal to: $\alpha_1 = 7.91 \cdot 10^{-6}$ deg^{-1}, $\alpha_2 = 1.12 \cdot 10^{-5}$ deg^{-1} and $\alpha_3 = -3.48 \cdot 10^{-6}$ deg^{-1}. According to the relation between crystal and physical property symmetries [11], for the second rank tensor in the monoclinic crystal, the α_2 coefficient corresponds to the expansion along the crystallographic b axis. The angle φ between the α_1 axis and the a^* crystallographic axis is equal to 63.3°. The orientation of the thermal expansion eigenvectors with respect to the crystallographic axes is shown in Fig. 2. The thermal expansion of the crystal is highly anisotropic. The mean values of the linear thermal expansion coefficient defined as: $1/3(\alpha_1 + \alpha_2 + \alpha_3)$ is equal to $5.2 \cdot 10^{-6}$ deg^{-1} . This value is slightly larger than the values cited in [1] and [2] for the ceramic materials based on $CaAl_4O_7$.

It is very difficult to correlate the anisotropic thermal expansion of $CaAl_4O_7$ with its crystal structure. Fig. 2, 3 and 4 show the (*ac*), (*ab*) and (*bc*) views of the $CaAl_4O_7$ crystal structure, respectively. The crystal shows a typical inorganic structure with dense network of covalent bonds. The largest (but not large) expansion occurs along the crystallographic *b* axis, which seems to correspond to the direction of the densest packing. The negative expansion coefficient corresponds to the direction of empty channels in the atomic network. The thermal expansion of the crystal, being small, is not negligible. The observed decrease of the thermal expansion in the ceramic materials based on $CaAl_4O_7$ [1,2] results probably from their structures achieved in course of the technological processes.

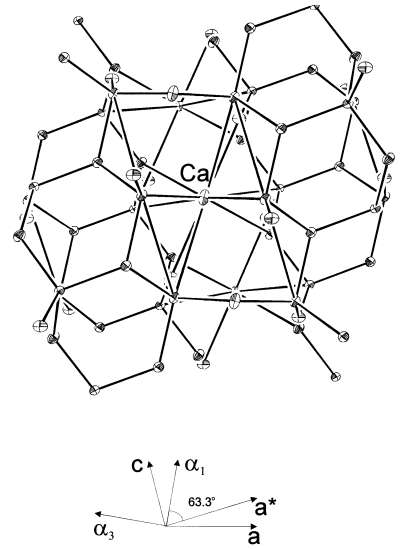

Figure 2. The ORTEP [11] (*ac*) view of the crystal structure with the orientation of the principal axes of the thermal expansion tensor with respect to the crystallographic axes.

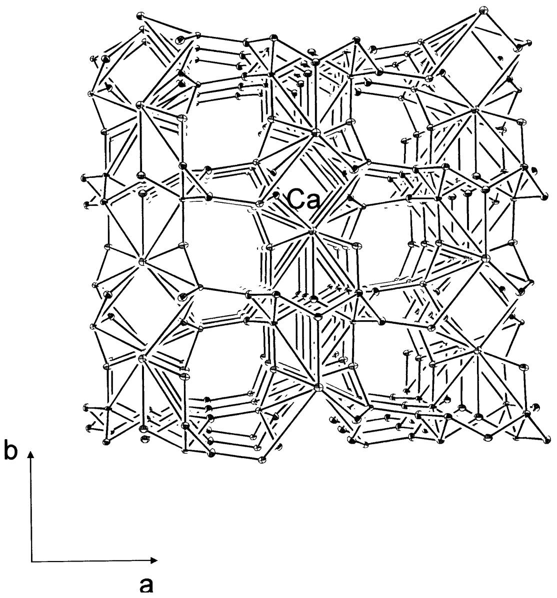

Figure 3. The ORTEP [11] (*ab*) view of the crystal structure.

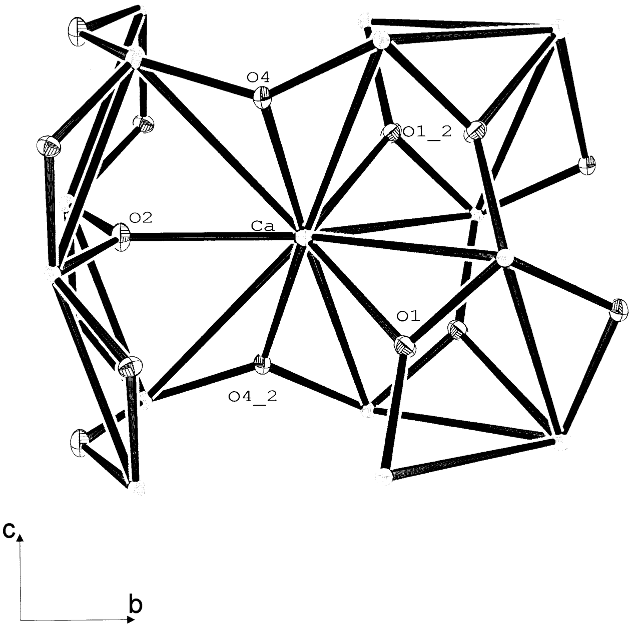

Figure 4. The ORTEP [11] (*bc*) view of the crystal structure.

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