

# High temperature thermal expansion of mullite: an in situ neutron diffraction study up to 1600°C

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## Abstract

Structural thermal expansions of undoped and Cr-doped 3/2 mullites (10.8 wt.% Cr<sub>2</sub>O<sub>3</sub>) were measured with in situ neutron (25–1600°C) and X-ray synchrotron (25–1000°C) diffraction techniques. Heat treatments between 25 and 300°C cause little and non-linear structural expansions. Above 300°C and up to 1000°C the mullites display linear and low increase of the lattice constants. The mean values of undoped mullite are slightly higher ( $\bar{\alpha}_{av} \approx 5.45 \times 10^{-6}$ ) than those of Cr-doped mullite ( $\bar{\alpha}_{av} \approx 4.95 \times 10^{-6}$ ), thus confirming earlier in situ high-temperature diffraction data. Above about 1000°C the expansion behaves discontinuously. Structural expansions of undoped and Cr-doped mullite strongly increase yielding similar mean expansion coefficients ( $\bar{\alpha}_{av} \approx 7.50 \times 10^{-6}$ ) for both materials. The highest increase of lattice constants has been determined in *b* axis direction throughout 1600°C in undoped and Cr-doped mullite. High temperature diffraction studies under heating-up and cooling-down conditions yielded reversible expansion effects, including the anomalous behaviour at about 1000°C. © 2001 Elsevier Science Ltd. All rights reserved.

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## 1. Introduction

Mullite is very rare in nature: it occurs in rocks of the sanidine- and corundum-sillimanite facies, at the contact of super heated volcanic intrusions, and in post volcanic hydrothermal formations. Mullite is named after the Isle of Mull (Scotland), where it was first described in nature. In spite of its rareness in natural rocks there is perhaps no mineral phase, which is regarded to be so basic in ceramics such as mullite. The outstanding position of mullite is documented by a huge number of scientific and technical papers, published during recent years. Of particular value in this context are the review articles by Davis and Pask,<sup>1</sup> Aksay et al.<sup>2</sup> and Schneider et al.<sup>3</sup> The importance of mullite in traditional and advanced ceramics can be explained by the material properties: low density, high thermal stability, stability in severe chemical environments, low thermal conductivity and favourable strength and creep behaviour. A most important feature of mullite and mullite ceramics, explaining its high temperature shape stability and excellent thermal shock resistance, is the low thermal expansion. Structure-resolved thermal expansion data

of undoped sinter-mullite and fused-mullite, and of Cr-doped (11.5 wt.% Cr<sub>2</sub>O<sub>3</sub>) and Fe-doped sinter-mullite (10.3 wt.% Fe<sub>2</sub>O<sub>3</sub>) were collected by means of high precision Guinier X-ray diffraction measurements between room temperature and 900°C.<sup>4</sup> These measurements confirmed the low mean linear expansion coefficient of mullite ( $< 5.5 \times 10^{-6}$ ) as determined by dilatometry. X-ray Guinier powder and single crystal studies (Bond method) indicated that mullite displays slight changes of the expansion curve slopes between about 400 and 500°C.<sup>5</sup>

Dilatometric expansion data of ZrO<sub>2</sub> particle reinforced mullite composites with reference to monophase mullite up to about 1200°C were published by Ishitsuka et al.<sup>6</sup> There exists a relationship between thermal expansion and the ZrO<sub>2</sub> content of the composite. A direct relationship also exists between thermal expansion and phase content of cordierite/mullite and teillite/mullite composites.<sup>7</sup> These materials are interesting, because cordierite and teillite both display thermal expansion coefficients close to zero. They are, therefore, suitable materials for high performance catalyst converters in automotive and diesel engines. However, these materials suffer from very low mechanical strength, while composites made of mullite and cordierite or teillite, respectively, display much better mechanical behaviour.

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## 2. Experimental

### 2.1. Sample material

Mullite powders were synthesized from chemically pure  $\text{Al}_2\text{O}_3$  (VAW 302),  $\text{SiO}_2$  (Ventron 88316), and  $\text{Cr}_2\text{O}_3$  (Merck 2483) powders with (70– $x$ ) wt.%  $\text{Al}_2\text{O}_3$  and 30 wt.%  $\text{SiO}_2$ , either with pure ( $x=0$ , designated as undoped mullite) or with 10 wt.%  $\text{Cr}_2\text{O}_3$  ( $x=10$ , designated as Cr-doped mullite). The carefully homogenized powders had mean grain sizes of about 5  $\mu\text{m}$ . The powder mixtures were pressed to 20 mm diameter  $\times$  5 mm height disks in a pressing mold using uniaxial pressure loading. Samples were reaction-sintered at 1650°C for 72 h. All experiments were carried out in a laboratory furnace in air at 1 atm. After the synthesis procedure the samples consisted of mullite and a minor amount of coexisting glass plus  $\alpha$ - $\text{Al}_2\text{O}_3$  (undoped sample) and glass (Cr-doped sample), respectively. According to EDX measurements, carried out with a scanning electron microscope (LEO Gemini 982) the following chemical compositions were determined: undoped mullite:  $\text{Al}_2\text{O}_3$ : 71.4 wt.%,  $\text{SiO}_2$ : 28.6 wt.%, and Cr-doped mullite:  $\text{Al}_2\text{O}_3$ : 60.4 wt.%,  $\text{SiO}_2$ : 28.8 wt.%,  $\text{Cr}_2\text{O}_3$ : 10.8 wt.%. These values correspond to a structural state close to the value of 3/2-mullite for both mullites investigated.

### 2.2. High temperature diffraction studies

High temperature lattice parameters of undoped and Cr-doped mullites were determined with neutron and X-ray (synchrotron-) diffractometry in situ at temperatures up to 1600°C. Most of the in situ high temperature studies were carried out by means of neutron diffractometry. Compared to X-ray diffraction the essential advantages of the neutron diffraction method are as follows: (i) easier experimental work at high temperature, in particular above 1000°C, due to low absorption of thermal neutrons by the materials of the diffraction furnace. As a consequence, there is a lower spurious background scattering which might obscure weak diffraction signals; (ii) a special mirror furnace which offers the possibility to work with relatively “large” (ceramic) samples (up to sizes of the order of 1 cm) in oxidizing atmosphere; (iii) neutrons provide a better scattering contrast of the constituent elements (Al, Si, O) of mullite; (iv) due to the absence of a significant absorption and atomic form factor influence, usually being the main source of systematic errors in X-ray work, more reliable temperature coefficients and atomic displacement parameters can be achieved from neutron diffraction results. On the other hand, the highly collimated brilliant X-ray beams which are available with synchrotron (X-ray) sources, provide an extremely good angular resolution being superior to the experimental conditions in the neutron case. Such synchrotron mea-

surements were carried out on Cr-doped mullite between 25 and 1000°C.

The lattice parameters were derived from full structure refinements, based on neutron (and X-ray) data using the Rietveld technique. The lattice constants thus are the result of the optimized matching of refinable parameters with respect to the observed positions and intensities of all reflections. Various programs are available world-wide, actually the program “FULLPROF”<sup>8</sup> was used in this work. It should be emphasized, however, that results obtained by the use of different programs do not differ much with respect to the final values of the lattice constants. In the present case, typical quality factors such as the reliability (“R”-) factor were around 7% and the so-called gof-values (“goodness-of-fit”) scattered around 1.8. This indicates highly reliable lattice constants. For a more detailed discussion of all aspects of structural refinements, the reader is referred to the forthcoming paper on the high temperature structure of mullite by Brunauer and coworkers.<sup>9</sup>

The high temperature neutron diffraction experiments were performed at ILL/Grenoble ( $\lambda=0.15938$  nm) and at BENSC/HMI-Berlin ( $\lambda=0.17964$  nm) in an ellipsoid mirror furnace.<sup>10</sup> About 20 min were allowed to stabilize the temperature in both “heating-up” and “cooling-down” cycles prior to diffraction runs. A temperature stability of  $\pm 2$  K was achieved during the measurements, which lasted 9–10 h each. The temperature measurements were performed with a PtRh30–PtRh10 thermocouple which was introduced into the platinum sample container. In the synchrotron radiation high temperature experiments at HASYLAB/Desy-Hamburg ( $\lambda=0.1267$  nm) a STOE furnace with a graphite heating tube was used. The experiments were carried out in vacuum. The temperature stability was about  $\pm 2$  K and the duration of diffraction runs was 9–10 h similar to conditions of the neutron diffraction studies.

## 3. Results

In-situ high temperature neutron and X-ray diffractometer runs show that after a non-linear induction period with very little expansion below about 300°C, undoped and Cr-doped mullites display linear and relatively low expansions of and  $a$ ,  $b$ ,  $c$  lattice constants and cell volume (Fig. 1a–d). At about 1000°C a distinct and anomalous change of the slopes occurs in both mullite compositions. Above this critical temperature and up to the maximum temperature of 1600°C the expansion curves are linear again, but with significantly steeper slopes than below 1000°C, corresponding to higher  $\alpha(a)$ ,  $\alpha(b)$  and  $\alpha(c)$  expansion coefficients (Table 1). The temperature-induced  $a$  and  $b$  expansions of undoped mullite below 1000°C determined with neutron diffraction match well with synchrotron radiation measurements

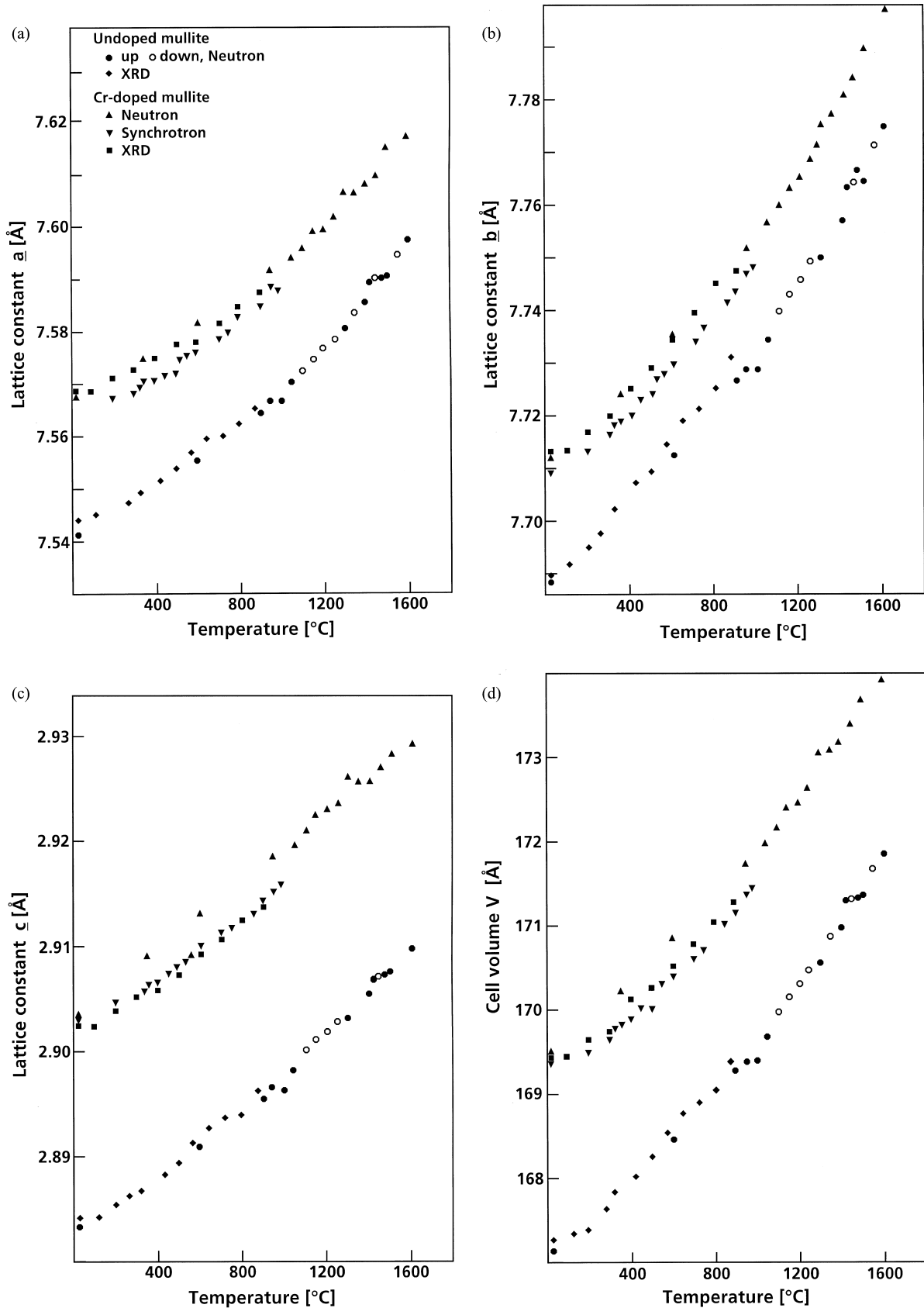


Fig. 1. Change of lattice constants  $a$ ,  $b$  and  $c$  and cell volume  $V$  with temperature. The mean quadratic errors of the lattice constants are below the width of symbols. Specified temperature-dependent lattice parameters of the mullites can be made available on request. Neutron: data on the basis of neutron diffraction. Synchrotron: data on the basis of synchrotron radiation. XRD: data on the basis of X-ray diffraction. Up: heating-up runs. Down: cooling-down runs.

Table 1  
Temperature-induced structural expansion of mullite

Mullite sample	Temperature range (°C)	Expansion coefficients ( $\times 10^{-6}/^{\circ}\text{C}$ )					Anisotropy factor		Reference
		<i>a</i> -axis $\alpha(a)$	<i>b</i> -axis $\alpha(b)$	<i>c</i> -axis $\alpha(c)$	Mean $\bar{\alpha}^a$	$\bar{\alpha}^b$	$A^c$	$\frac{A}{\bar{A}^d}$	
Undoped	300–1000	4.1	6.0	5.7	5.3	5.45	3.8	5.0	This study
		3.9	7.0	5.8	5.6		6.2		Schneider and Eberhard <sup>4</sup>
	1000–1600	6.8	9.3	6.3	7.5	7.50	6.0		This study
Cr-doped	300–1000	3.6	5.9	5.2	4.9	4.95	4.6	5.4	This study
		3.1	6.2	5.6	5.0		6.2		Schneider and Eberhard <sup>4</sup>
	1000–1600	5.8	11.0	6.1	7.6	7.60	10.4		This study

<sup>a</sup> Mean thermal expansion coefficients are given by  $\bar{\alpha} = (\alpha(a) + \alpha(b) + \alpha(c))/3$ .

<sup>b</sup> Average thermal expansion coefficients ( $\bar{\alpha}_{av}$ ) calculated from neutron and XRD data.

<sup>c</sup> Anisotropy factor  $A$  of thermal expansion given by  $A = (|\alpha(b) - \alpha(c)| + |\alpha(b) - \alpha(a)| + |\alpha(c) - \alpha(a)|) \times 10^{-6}$  calculated from neutron and XRD data

<sup>d</sup> Average anisotropy factors  $\bar{A}$ .

(this study) and with in situ X-ray diffraction derived data up to 900°C,<sup>4</sup> while temperature-dependent *c* constants determined on the basis of synchrotron radiation and X-ray diffraction tend to be lower than neutron diffraction data (Fig. 1a–c). The diffraction studies yielded similar tendencies for both undoped and Cr-doped mullite: Highest thermal expansions occur in *b* axis direction [ $\alpha(b)$ ] throughout 1600°C. Expansions along *a* and *c* are different: Below 1000°C *c* expansions [ $\alpha(c)$ ] are distinctly higher than *a* expansions [ $\alpha(a)$ ], while above 1000°C both values become similar (Table 1). High temperature diffraction studies under “cooling-down” conditions yield lattice spacings very similar to those of the “heating-up” cycles at a given temperature, thus indicating very little hysteresis of “up” and “down” expansion curves. This proves that thermal expansion, including the “expansion discontinuity” at about 1000°C is reversible.

Mean thermal expansion coefficients were calculated on the basis of  $\bar{\alpha} = (\alpha(a) + \alpha(b) + \alpha(c))/3$  from diffraction data (Table 1). Values are slightly smaller for Cr-doped ( $\bar{\alpha}_{av} \approx 4.95$ ) than for undoped mullite ( $\bar{\alpha}_{av} \approx 5.45$ ) below 1000°C.<sup>4</sup> Above 1000°C both mullite compositions display similar  $\bar{\alpha}$  values, being significantly higher ( $\bar{\alpha}_{Cr} \approx \bar{\alpha}_{un} \approx 7.5$ ) than below 1000°C. Structure-controlled thermal expansion anisotropies of mullite were calculated according to the formalism of Schneider and Eberhard:<sup>4</sup>  $A = (|\alpha(b) - \alpha(c)| + |\alpha(b) - \alpha(a)| + |\alpha(c) - \alpha(a)|) \times 10^{-6}$ . For undoped mullite the  $A$ -value increases only slightly from 5.0 (<1000°C) to about 6.0 (>1000°C). In contrast, the  $A$ -value of Cr-doped mullite increases much stronger from about 5.4 below 1000°C to about 10.4 above 1000°C, indicating a strong anisotropy.

#### 4. Discussion

Our in situ high temperature neutron diffraction study for the first time provides exact structure-resolved thermal expansion values of mullite in the high temperature range between 900 and 1600°C. There exists an expansion

anomaly at about 1000°C, which may be correlated with a second order reversible phase transition. In situ high temperature Raman and optical absorption spectroscopy and heat capacity ( $c_p$ ) measurements provide evidence for this approach (unpublished data). The temperature-dependent development of lattice constants, however, can also be fitted with a continuous curve of the type  $\text{const} + aT + bT^2$  (C. Rüscher, pers. commun.). A detailed structural discussion including interatomic distances and cation–oxygen–cation angles will be given in a separate paper.<sup>9</sup>

Mullite displays low mean thermal expansion below 1000°C (undoped mullite:  $\bar{\alpha} \approx 5.45$ , Cr-doped mullite  $\bar{\alpha} \approx 4.95$ ). The lower expansion makes Cr-doped mullite a suitable material for applications below 1000°C, if shape stability and high thermal shock resistance of components are required. Above 1000°C, both undoped and Cr-doped mullite display similar, but higher mean expansion values (undoped mullite  $\approx$  Cr-doped mullite:  $\bar{\alpha}_{av} \approx 7.50$ ). If thermal shock resistance from temperatures above 1000 to below 1000°C is taken into account, undoped mullite may be the better choice, since the difference of mean thermal expansion coefficients  $\Delta\bar{\alpha}$  above and below 1000°C is smaller than that of Cr-doped mullite (undoped mullite:  $\Delta\bar{\alpha} \approx 2.0$ , Cr-doped mullite:  $\Delta\bar{\alpha} \approx 2.6$ ). Schneider and Eberhard<sup>4</sup> believed that the non-linear thermal expansion below 300°C should not be explained with the low thermal conductivity of mullite, since the time of temperature exposure in their experiments was more than sufficient to achieve temperature equilibrium. A better explanation may be the low thermal energy below 300°C which is simply not high enough as to initiate expansion.

The structure-controlled expansion anisotropy of phases is an important factor to predict the temperature behaviour of ceramics. The expansion anisotropy is only slightly different for undoped ( $A \approx 5.0$ ) and Cr-doped mullites ( $A \approx 5.4$ ) below 1000°C. On the other hand, above 1000°C the anisotropy factor of Cr-doped mullite ( $A \approx 10.4$ ) is much higher than that of undoped

mullite ( $A \approx 6.0$ , Table 1). This provides further evidence that Cr-doped mullite is less favourable for ultra-high temperature applications under cycling conditions as compared to undoped mullite, especially in ceramics with preferred orientation of mullite crystals (e.g. templated grown mullite).<sup>11</sup>

The present study confirms the favorably low thermal expansion of mullite, providing good shape stability with temperature change (“near-net-shape”) and high thermal shock resistance. It makes mullite an excellent material for catalysator converters, burner tubes and kiln furnitures, and, if reinforced by ceramic fibers, a very good damage tolerant matrix for ceramic composites for long-term high temperature uses, e.g. in gas turbine engines.

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