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Complete List of Authors:	<p>Murshed, M. Mangir; Chemical Crystallography for Solid State Materials, Institute of Inorganic Chemistry and Crystallography; MAPEX Center for Materials and Processes, Bibliothekstraße 1, Universität Bremen, D-28359</p> <p>Sehovic, Malik; Chemical Crystallography for Solid State Materials, Institute of Inorganic Chemistry and Crystallography; MAPEX Center for Materials and Processes, Bibliothekstraße 1, Universität Bremen, D-28359</p> <p>Fischer, Michael; Kristallographie, FB Geowissenschaften, Universität Bremen, Klagenfurter Straße, Universität Bremen, D-28359; MAPEX Center for Materials and Processes, Bibliothekstraße 1, Universität Bremen, D-28359</p> <p>Senyshyn, Anatoliy; Research neutron reactor ZWE FRM-II, Munich University of Technology, Lichtenbergstrasse 1, D-85747</p> <p>Schneider, Hartmut; Kristallographie, FB Geowissenschaften, Universität Bremen, Klagenfurter Straße, Universität Bremen, D-28359</p> <p>Gesing, Thorsten; Chemical Crystallography for Solid State Materials, Institute of Inorganic Chemistry and Crystallography; MAPEX Center for Materials and Processes, Bibliothekstraße 1, Universität Bremen, D-28359</p>
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Thermal behavior of mullite between 4 K and 1320 K

M. Mangir Murshed^{1,2*}, Malik Šehović^{1,2}, Michael Fischer^{2,3}, Anatoliy Senyshyn⁴,
Hartmut Schneider³, Thorsten M. Gesing^{1,2}

¹Chemische Kristallographie fester Stoffe, Institut für Anorganische Chemie und Kristallographie, FB Biologie/Chemie, Universität Bremen, Leobener Straße /NW2, D-28359 Bremen, Germany

²MAPEX Center for Materials and Processes, Bibliothekstraße 1, Universität Bremen, D-28359 Bremen, Germany

³Kristallographie, FB Geowissenschaften, Universität Bremen, Klagenfurter Straße, Universität Bremen, D-28359 Bremen, Germany

⁴Research neutron reactor ZWE FRM-II, Munich University of Technology, Lichtenbergstrasse 1, D-85747 Garching, Germany

*Corresponding author Tel.: +49 (0)421 218 63144, fax: +49 421 218 63145.; e-mail: murshed@uni-bremen.de

Abstract

The evolution of metric parameters of 2:1 and 3:2 mullites have been measured between 4 K and 1320 K using neutron and X-ray powder diffraction. Negative thermal expansion was observed at low temperature for the *a*-cell parameter and consequently for the cell-volume, which is more pronounced for 2:1 mullite than those for 3:2 mullite. Each parameter is simulated using Grüneisen first-order approximation for the zero pressure equation of state at 0 K, where the vibrational energy was calculated using microscopic approach. While the *b*- and *c*-cell parameters require only one Debye term, a second Debye spectrum with negative Grüneisen parameter was required to fit the *a*-cell parameter as well as the cell volume. Temperature-dependent Raman spectra and phonon density of states hint for the possible microscopic sources of the cell contraction at low temperature. A simple polynomial approach is presented to calculate the elastic stiffness of the 3:2 mullite for the determination of the axial Grüneisen parameter.

Keywords: mullite, thermal expansion, phonon, neutron diffraction, X-ray diffraction

1. Introduction

Mullite with chemical composition $\text{Al}_2[\text{Al}_{2+2x}\text{Si}_{2-2x}]\text{O}_{10-x}$ is perhaps one of the most widely studied Al_2O_3 - SiO_2 systems because of its useful properties such as thermal stability, low thermal expansion, low thermal and electrical conductivity, excellent creep resistance [1]. The reported composition varies between $x = 0.18$ and $x = 0.88$ corresponding to 57 mol% and 92 mol% Al_2O_3 , respectively [2], however, the most frequently occurring phases are $x = 0.25$ (3:2 mullite, also named as sintered mullite) and $x = 0.40$ (2:1 mullite, also named as fused mullite). The 3:2-phase is known as mullite in the strict sense, which has been drawn research interests to interdisciplinary communities concerned to crystal structure, crystal chemistry and related properties, the stability of mullite and theoretical studies. Many investigations were extended on the fabrication and tailoring the properties for applications of both traditional and advanced mullite ceramics [3, 4]. The crystal structure of mullite is shown in figure 1, which can be better described in terms of the closely related sillimanite (Al_2SiO_5) structure [1, 2]. The edge-sharing AlO_6 octahedra run parallel to the *c*-axis and are cross-linked by strictly ordered AlO_4 - SiO_4 (T_2O_7) double-tetrahedra. Any disordering ensures a statistical distribution of $(\text{Al},\text{Si})_2\text{O}_7$ double-tetrahedra forming the disordered sillimanite corresponding to hypothetical 1:1 mullite ($x = 0$) with half the *c*-cell parameter. Mullite can be derived from sillimanite by the mechanism: $2\text{Si}^{4+} + \text{O}^{2-} = 2\text{Al}^{3+} + \text{vacancy}$; thus *x* in $\text{Al}_2[\text{Al}_{2+2x}\text{Si}_{2-2x}]\text{O}_{10-x}$ composition directly counts the number of vacancies. The oxygen atom (O3, also designated as 'Oc') bridging the AlO_4 and SiO_4 tetrahedra has been removed. As a consequence the tetrahedral T-sites (T) displace to a new position (T3, also designated as T*) followed by formation of T_3O -tricluster ($\text{T}_2\text{T}^*\text{O}_4$, Fig. 1) where the associated O3-atom slightly shifts from its special position ($2d; 0, \frac{1}{2}, \frac{1}{2}$) to O4 (also designated as Oc*). In the same manner formation of a T_4O -tetracluster ($\text{O}_4\text{T}_2\text{T}^*_2$) is also known to exist in

mullites with $x > 0.67$ [2]. Whereas mullite is known since many years [1] and more than three thousand relevant publications are available, the understanding of its crystal and physico-chemical properties at low temperatures are surprisingly limited; for instance, a systematic study at low temperature is still missing. Since mullite is a typical compound of high-temperature ceramics its thermal expansion was studied [5] only at high temperatures. In many cases the high-temperature metric parameters were extrapolated down to 0 K to have a guideline for theoretical calculations [6]. However, discrepancy in the metric parameters is marked perhaps due to lack of low-temperature data and the associated non-linear thermal expansion.

Figure 1: Crystal structure of a hypothetical mullite showing AlO₄/SiO₄ tetrahedra and AlO₆ octahedra and their connectivity along with T₃O-triclusters and T₄O-tetraclusters formed due to oxygen vacancies (□) on the O3 position.

Although Al_2O_3 has excellent mechanical and electrical properties its commercial application is restricted due to its poor thermal shock resistance (TSR) [1]. Since mullite has excellent TSR the high-alumina containing mullite can serve for a ceramic with improved TSR for potential usages. The thermoelastic properties of mullites at low temperatures are not available, and the role of the structural vacancies (Fig. 1) even of mostly studied mullites is unclear. It is therefore of crucial importance to have accurate structural insights of mullites with different Al/Si ratio at low temperatures. Here we report the thermal behaviors of 2:1 and 3:2 mullites between 4 K and 1320 K.

The cation in the tetrahedral T-site triggered a marked controversy. It was demonstrated that the occupancy of these T-sites with silicon is either very small or even zero [2, 3]. Due to the presence of T_3O - and T_4O -clusters in mullites (T_3O for $x < 0.67$ and, T_3O - and T_4O for $x > 0.67$) the in-house X-ray diffraction can hardly resolve the structural details as four Wyckoff sites are partially occupied. The light oxygen atoms and their disordering at O4-site (molecular dynamics simulation) suggests oxygen hops between O3- and O4-sites [7]), the similar X-ray scattering of Al^{3+} and Si^{4+} harbor additional structural pitfalls in mullites with respect to the compositional x . Therefore the present study bears particular importance of accurate temperature-dependent crystal structure for a broad range. There exists a scarcity of theoretical works on mullites [6], either on thermodynamics or mechanical properties due to complexity and the disordered nature of the structure. Moreover, necessity of a large supercell to cope with the partially occupied sites adds considerable computational costs for an accurate calculation. The present study also deals with large supercells using empirical potentials, where five models are presented (each model comprises of a distinct distribution of vacancy and disordering), leading to different mechanical properties and their relations to the alumina content in the structures.

2. Experimental

2.1. Synthesis

The 3:2 mullite powder was synthesized using aluminum sec-butoxide ($\text{Al}(\text{OC}_4\text{H}_9)_3$) and tetraethyloxysilane ($\text{Si}(\text{OC}_2\text{H}_5)_4$). After dilution of the starting materials in isopropanol it was heated at 1873 K for 2h. The 2:1 mullite was produced from Al_2O_3 and SiO_2 powders followed by electric arc furnace of Washington Mills Electro Minerals Ltd. The fusion was performed at about 2273 K. The 2:1 mullite contains about 0.2 wt% Na_2O and traces of Fe_2O_3 and TiO_2 . More details of the syntheses of relevant mullites are available elsewhere [1].

2.2. Neutron and X-ray diffraction

Neutron powder diffraction

Temperature-dependent neutron powder diffraction (NPD) experiments were carried out between 4 K and 320 K with a temperature slice of 10 K on the high-resolution powder diffractometer SPODI [8] at FRM-II, Germany. A collimated beam of thermal neutrons ($\lambda = 154.812(2)$ pm) has been obtained at a take-off angle of 155° using the (551) reflection of a vertically focusing composite germanium monochromator. Data were collected in the 2θ range between 1° and 152° with a step size of 0.05° .

X-ray powder diffraction

High-temperature X-ray powder diffraction (XRPD) measurements were carried out for the synthesized powder products followed by structure refinements with the fundamental parameter approach using the “Diffra^{Plus} Topas 4.2” (Bruker AXS GmbH, Karlsruhe) software. Data were collected on a Bragg-Brentano PANalytical X’Pert MPD PRO diffraction system (PANalytical

GmbH, Almelo, The Netherlands) equipped with a secondary Ni filter, CuK α radiation and an X'Celerator multi-strip detector using an HTK 1200N heating chamber (Anton Paar, Graz, Austria). The sample was prepared in a flat corundum sample holder using acetone to submerge the mullite powder and to produce small evaporation channels which served as an additional space for the thermal expansion of the compound. A conventional glass slide was used for pressing and shaping the sample and to restrain the vapor pressure of the acetone and therefore hamper the formation of drying cracks by placing it slightly above the sample surface during the drying process. Measurements were carried out between 300 K and 1330 K in steps of 10 K. Each pattern was recorded from 10° to 130° 2 θ with a step size of 0.0167° and a 90 s/step total data collection time. For the Rietveld refinement the starting atomic coordinates were taken from the room-temperature single crystal X-ray data of 2:1 mullite [9]. All refinements were performed via batch treatments, where the last refinement result served as a starting model for the following calculation. Special care was taken on the temperature accuracy of the in-house XRPD measurements. On the basis of the thermal expansion of pure Si and, Si mixed with the respective mullite using a ratio of 1:1, the refined metric parameters are comparable with values from Okada and Tokumaru [10] as shown in figure 2. The observed cell parameter of Si in the region of interest slightly deviates from that of the reliable dataset [10]. Subsequently the mixed samples, measured in the temperature range of 300 K – 320 K, were used to slightly adjust the respective NPD wavelength. The composite data collected from low-temperature NPD and high-temperature XRPD were used to study the lattice thermal expansion of the mullites.

Figure 2: Temperature-dependent metric parameter of standard Si, and Si mixed with mullites (1:1).

2.3. Raman spectroscopy

The temperature-dependent Raman spectra were recorded on a LabRam ARAMIS (Horiba Jobin Yvon) Micro-Raman spectrometer equipped with a laser working at 785 nm and less than 20 mW. A 50x long working distance objective (Olympus) with a numerical aperture of 0.55 provides a focus spot of about 2 μm diameter when closing the confocal hole to 200 μm . Raman spectra were collected in the range 80 cm^{-1} to 1500 cm^{-1} with a spectral resolution of approximately 1.0 cm^{-1} using a grating of 1800 grooves/mm and a thermoelectrically-cooled CCD detector (Synapse, 1024 x 256 pixels). The spectral positions were calibrated against the Raman mode of Si ($520.7 \pm 0.1\text{ cm}^{-1}$) before and after the sample measurements. Moreover, the linearity of the spectrometer was calibrated against the emission lines of a neon lamp. For the low-temperature measurements, a pressed-pellet (5 mm^3) was placed on a Linkam cooling stage (THMS600) attached to a pump (LNP95 Cooling Pump) that provides a continuous flow of liquid nitrogen. The measurements were carried out between 80 K and 300 K at each 10 K. A

ramp rate of 1/12 K/s and a holding time of 300 s were followed to properly equilibrate the temperature. The high-temperature spectra were performed between 300 K and 500 K placing the pellet into a Linkam heating stage (TS1500) using temperature steps of 10 K, a heating rate of 1/12 K/s and a holding time of 300 s prior to the data collection. In both cases the temperature was stable within ± 0.1 K at each measuring temperature. For temperature-dependent data analysis each spectrum was baseline corrected and fitted (Pseudo-Voigt) with the 'LAMP' software [11] that allowed for a precise determination of the band positions and line-width. Deconvolution of some spectral parts, due to overlapping with increasing temperature, into single Pseudo-Voigt components was also carried out within the LAMP facilities.

2.4. Theoretical calculations

Empirical-potential calculations were performed using the GULP code [12]. In order to account for the disordering in mullites, five models were prepared for 2:1 mullite as well as for 3:2 mullite. Each model differs from the other in the arrangement of the oxygen vacancy (O3) and the positions of tetrahedrally coordinated T-sites. For 2:1 mullite, a $2 \times 2 \times 5$ supercell was used, and a total of eight O3-atoms per supercell were removed using a random algorithm, however avoiding oxygen vacancy in the adjacent positions. Correspondingly, a $2 \times 2 \times 4$ supercell was used for 3:2 mullite, where four O3-atoms per supercell were removed using the same strategy as for the 2:1 mullite. The Al- and Si-atoms were distributed over the tetrahedral T-positions to arrive at the correct stoichiometry, while the T3-sites were assumed to be exclusively occupied by Al. The GULP optimizations were performed at fixed lattice dimensions. To account for the effect of temperature, separate sets of calculations were performed using the experimentally obtained metric parameters at 4 K, 300 K, 600 K, 900 K, and 1200 K as listed in table 1. The calculations used a set of potential parameters devised by Winkler et al. [13], which were validated for

aluminosilicate minerals. The parameter set is largely based on some earlier works [14, 15]. Additionally, the O-Al-O bending term was included, which explicitly distinguishes between tetrahedrally and octahedrally coordinated Al-atoms. The phonon density of states (PDOS) and the elastic stiffness coefficients were obtained from the GULP calculations for each individual model. In order to better approximate the bulk properties of the mullites, averaged quantities were obtained from the respective values of the individual models.

Table 1: Temperature-dependent metric parameters of 2:1 and 3:2 mullites.

2:1 mullite					3:2 mullite				
T /K	a /pm	b /pm	c /pm	$V/10^6$. pm ³	a /pm	b /pm	c /pm	$V/10^6$. pm ³	Diffraction
4	757.628(9)	768.287(8)	288.539(3)	167.952(2)	755.212(11)	769.199(10)	288.454(3)	167.566(3)	NPD
300	757.683(10)	768.624(9)	288.657(3)	168.106(2)	755.340(11)	769.530(10)	288.553(4)	167.724(3)	NPD
300	757.683(10)	768.624(9)	288.657(3)	168.106(2)	755.340(11)	769.530(10)	288.553(4)	167.724(3)	XRPD
600	758.286(9)	769.754(6)	289.076(3)	168.732(3)	756.081(12)	770.628(11)	288.930(3)	168.347(4)	XRPD
900	759.174(9)	771.104(6)	289.590(3)	169.527(3)	757.019(12)	771.950(11)	289.395(4)	169.117(4)	XRPD
1200	760.150(9)	772.508(6)	290.138(3)	170.375(3)	758.119(12)	773.391(12)	289.913(4)	169.982(4)	XRPD

NPD and XRPD refer to neutron powder diffraction and X-ray powder diffraction, respectively. Value in the parenthesis is the respective estimated standard deviation. An uncertainty of ± 1 K temperature for the XRPD was estimated to be taken into account.

3. Results and discussion

3.1. Elastic property

Temperature-dependent nine independent stiffness coefficients of the 2:1 and 3:2 mullites are shown in figure 3. The calculated each elastic stiffness of 2:1 mullite shows a deviation from the experimentally observed corresponding one at room temperature [16], however, the order ($c_{33} > c_{22} > c_{11} > c_{23} > c_{44} > c_{12} > c_{66} > c_{55}$) of the averaged values for both 2:1 and 3:2 mullites are

Figure 3: Temperature-dependent elastic stiffness of 2:1 (top) and 3:2 (bottom) mullites.

consistent with the experimental ones at any given temperature. Unfortunately, still the experimental values of the elastic stiffness coefficients of 3:2 mullite are either uncertain or not

available largely due to unavailability of suitable single crystal, thus a comparison cannot be made here. However, considering sillimanite ($x = 0$ [17]) on the one end and iota-alumina ($x = 1$ [18]) on the other end, the polynomial fitting of some available data provides an averaged model line for the elastic stiffness of the 3:2 mullite as shown in figure 4. The taken elastic stiffness and fitting parameters are given in table 2; bulk moduli for both mullites are also given for comparison.

Figure 4: Elastic stiffness versus compositional x in mullites. The shaded area shows 95% confidence bound for the polynomial fitting (solid line) of the data (table 2).

Table 2: Elastic stiffness (c_{ij}), fitting parameters and bulk moduli of $\text{Al}_{4+2x}\text{Si}_{2-2x}\text{O}_{10-x}$ mullites.

J. Am. Ceram. Soc.

<i>c_{ij}</i> /GPa										
x	<i>c₁₁</i>	<i>c₂₂</i>	<i>c₃₃</i>	<i>c₄₄</i>	<i>c₅₅</i>	<i>c₆₆</i>	<i>c₁₂</i>	<i>c₁₃</i>	<i>c₂₃</i>	Ref.
0	287.3	231.9	388.4	122.4	80.7	89.3	94.7	83.4	158.6	[17]
“-	283.5	230.7	405.4	114.5	74.2	82.6	110.1	105.60	131.3	[19]
0.25	265.3	233.8	373.6	104.3	73.6	82.3	106.9	115.90	138.8	[19]
0.39	291.3	232.9	352.1	110.3	77.39	79.9	112.9	96.22	121.9	[20]
“-	279.5	234.9	360.6	109.49	74.94	79.89	103.1	96.10	135.6	[16]
0.40	261.4	235.5	347.5	103.2	64.3	80.6	109.4	97.60	261.4	polyfit
0.50	280.0	245.	362.0	111.0	78.1	79.0	105.0	99.2	135.0	[21]
“-	281.9	244.2	363.6	111.7	78.2	79.2	105.1	100.30	142.3	[22]
0.67	219.2	220.7	298.6	97.1	69.5	61.8	93.9	101.20	128.5	[19]
0.84	172.3	174.6	271.3	79.3	59.2	63.3	79.9	78.50	104.2	[19]
1.00	196.0	208.8	264.9	84.3	60.6	76.6	97.0	91.40	117.7	[18]
Fitting parameters ($y = A_0 + A_1 * x + A_2 * x^2$)										
<i>A₀</i>	286.2	232.3	397.6	117.4	76.85	87.63	104.3	97.11	144.8	286.2
<i>A₁</i>	18.73	40.86	-72.39	-13.66	1.86	-28.76	15.21	21.46	-21.1	18.73
<i>A₂</i>	-132.9	-83.12	-71.69	-23.91	-20.07	10.24	-32.77	-34.19	-12.37	-132.9
Bulk modulus /GPa										
x	<i>K_{0a}</i>	<i>K_{0b}</i>	<i>K_{0c}</i>	<i>K_{0,R}</i>	<i>K_{0,V}</i>	<i>K_{0,VRH}</i>	Ref.			
0.25	461.34	386.98	884.57	170.00	176.13	173.07	polyfit			
“-	-	-	-	-	-	174.0	[23]			
“-	-	-	-	-	-	173.9	[24]			
“-	-	-	-	-	-	173(7)	[25]			
0.39	510.70	382.96	713.79	167.5	170.9	169.2	[20]			
“-	453.29	386.17	825.44	166.5	171.7	169.1	[16]			
0.40	446.75	390.81	827.15	166.50	171.60	169.05	polyfit			

K_{0a}, *K_{0b}*, and *K_{0c}* are axial bulk moduli in the crystallographic **a**-, **b**- and **c**-direction; *K_{0,R}*, *K_{0,V}*, and *K_{0,VRH}* are bulk modulus in Reuss, Voigt and Voigt-Reuss-Hill average, respectively.

The iota-alumina was considered as being the silica free phase possessing structural signatures of mullite, which is mechanically much softer than α -Al₂O₃ and γ -Al₂O₃ due to its ultralow density [18]. For instance, the elastic stiffness of iota-alumina along the principal directions are consistent with that of the characteristic order (*c₃₃* > *c₂₂* > *c₁₁*) in mullites. The gradual decrease

of each elastic stiffness parameter (Fig. 4) as well as the bulk moduli (Tab. 2) could be explained in terms of compositional x , that is, degree of disordering and associated vacancies. Our polynomial approach yields a bulk modulus of 173(1) GPa in the Voigt-Reuss-Hill approximation for the 3:2 mullite, which excellently agrees with the experimental ones (Tab. 2). Alike the experimental observations [16, 20] the longitudinal stiffness coefficient c_{33} is higher than those of c_{11} and c_{22} , leaving evidences of anisotropy for the axial stiffness. Anisotropy is also shown for the shear stiffness coefficients as c_{44} is higher than those of c_{55} and c_{66} , respectively, within the planes of (100), (010), and (001). Slight anisotropy can also be seen for the off-diagonal stiffness coefficients as c_{23} is higher than the counterpart c_{12} or c_{13} both for the 2:1 and 3:2 mullites. Variation of the stiffness coefficients between sillimanite and mullites are well explained elsewhere with respect to the corresponding crystal-chemistry [20]. Of particular notes, they described the higher c_{33} value mainly arises from the continuous *stiff* tetrahedral chains while the *soft* octahedral chains play a minor role. The decrease of the stiffness coefficient with increasing aluminum content (and therefore vacancy) in the mullite structure was also suggested to be due to weakening of the load-bearing tetrahedral chains parallel to the **c**-axis because of partial replacement of silicon by the weaker bonded aluminum [20]. The thermal conductivities of non-metallic solids directly correlate with their atomic bond strengths. For instance, the thermal conductivity of the purely covalent bonded diamond is the highest among all materials. As such, the elastic anisotropy is also reflected in the magnitude of thermal conductivity of 2:1 mullite [26]. The high thermal conductivity along the **c**-axis reflects the firmly bonded tetrahedral and octahedral chains running parallel to this direction. Since there is no strong structural chain in the **a**- and **b**-directions, the thermal conductivity at room temperature in these directions is about 2 W/mK less than that in the **c**-direction [26].

3.2. Thermal expansion

The XRPD and NPD data Rietveld refinement plots of the room-temperature data are shown in figure 5. Since low-temperature data are not available right now, representative structural parameters obtained from NPD at 4 K are given in table 3. The starting parameters for the Rietveld refinements were taken from the crystal structure of 2:1 mullites obtained from the single crystal X-ray diffraction [9]. The occupancy factors obtained by the

Figure 5: Rietveld plots of the 2:1 and 3:2 mullite data obtained from the neutron and X-ray diffractions at ambient pressure and 300(1) K.

Table 3: Low temperature (4 K) crystal structure data of 2:1 and 3:2 mullites obtained from neutron powder data Rietveld refinements.

2:1 mullite						
$a = 757.628(9) \text{ pm}$, $b = 768.287(8) \text{ pm}$, $c = 288.539(3) \text{ pm}$, $R_{wp} = 0.056$						
Atom	Designation	Site	Occupancy	x	y	z $B / \text{pm}^2 \cdot 10^4$
Al1	Al		1.0	0	0	0 1.85(4)
Al2	T		0.50	0.3514(2)	0.1594(2)	$\frac{1}{2}$ 2.54(4) ^b
Si2	T		0.331(1) ^a	0.3514(2)	0.1594(2)	$\frac{1}{2}$ 2.54(4) ^b
Al3	T*		0.169(3) ^a	0.2297(12)	0.2941(12)	$\frac{1}{2}$ 1.1(2)
O1	O(A,B)		1.0	0.1421(2)	0.0779(1)	$\frac{1}{2}$ 2.53(3)
O2	O(D)		1.0	0.3729(2)	0.2829(1)	0 2.44(3)
O3	O(C)		0.493(8) ^a	0	$\frac{1}{2}$	$\frac{1}{2}$ 3.5(1)
O4	O(C*)		0.169(3) ^a	0.0552(9)	0.4471(9)	$\frac{1}{2}$ 1.5(1)
3:2 mullite						
$a = 755.212(11) \text{ pm}$, $b = 769.199(10) \text{ pm}$, $c = 288.454(3) \text{ pm}$, $R_{wp} = 0.050$						
Al1	Al		1.0	0	0	0 1.56(4)
Al2	T		0.50	0.3510(1)	0.1590(2)	$\frac{1}{2}$ 2.11(3) ^b
Si2	T		0.352(1) ^a	0.3510(1)	0.1590(2)	$\frac{1}{2}$ 2.11(3) ^b
Al3	T*		0.148(1) ^a	0.2320(14)	0.2950(14)	$\frac{1}{2}$ 1.8(2)
O1	O(A,B)		1.0	0.1422(1)	0.0777(1)	$\frac{1}{2}$ 2.28(2)
O2	O(D)		1.0	0.3735(2)	0.2814(1)	0 2.25(2)
O3	O(C)		0.554(1) ^a	0	$\frac{1}{2}$	$\frac{1}{2}$ 2.84(8)
O4	O(C*)		0.148(1) ^a	0.0512(8)	0.4503(8)	$\frac{1}{2}$ 1.2(1)

^{a,b}Refinements were performed using the parameters constrained to each other.

NPD data (Tab. 3) show that the calculated x leads to composition $\text{Al}_{4.8(8)}\text{Si}_{1.2(8)}\text{O}_{9.2(8)}$ and $\text{Al}_{4.5(4)}\text{Si}_{1.5(4)}\text{O}_{9.75(5)}$, closely representing the ideal composition for 2:1 and 3:2 mullite, respectively. The metric parameters obtained from XRPD and NPD at some temperatures (300 K, 310 K and 320 K) are in excellent agreement within an adjustment of neutron wavelength of 154.812(2) pm. The evolution of metric parameters with increasing temperature is shown in figure 6.

Whereas the linear incompressibility follows the order as $K_c > K_b > K_a$ (Tab. 2), the axial thermal expansion coefficient (TEC) (α_a , α_b and α_c , respectively, for a -, b - and c -cell parameter) follows the order $\alpha_b > \alpha_c > \alpha_a$ at any given temperature, exhibiting violation of the empirical rule (the lowest thermal expansion occurs to the elastically stiffest crystal direction). This discrepancy was explained in terms of pure geometric considerations [27-29], however the underlying microscopic reason (local structure) is still unclear. Below 150 K slightly a negative thermal expansion is observed only in the **a**-direction of both 2:1 and 3:2 mullites. As a consequence the cell volume slightly shrinks at the given temperature region, which is clearly visible in the sensitive temperature-dependent thermal expansion coefficient (Fig. 6, insets). The electronic band gaps of 2:1 and 3:2 mullites ranges between ~ 7.7 eV and ~ 3.0 eV [19, [30]. Therefore, the thermal expansion excludes any electronic as well as ionic contribution, and can be explained purely from the lattice vibrational internal energy. In some recent reports we modeled the thermal expansion of mullite-type materials using Grüneisen first-order [31-34] and second-order [35] approximations for the zero-pressure equation of states. For the present study we consider the first-order approximation where the temperature-dependent metric parameter (M) can be expressed as:

$$M(T) = M_0 + \frac{\gamma U(T)}{K_0} \quad (1)$$

Figure 6a: Temperature-dependent metric parameters and thermal expansion coefficients of 2:1 mullite. The low-temperature data are shown (right) for better clarity.

Figure 6b: Temperature-dependent metric parameters and thermal expansion coefficients (inset) of 3:2 mullite. The low-temperature data are shown (right) for better clarity.

M_0 refers to metric parameter at 0 K, which possesses the zero-point energy. K_0 and γ are isothermal bulk modulus and thermodynamic Grüneisen parameter, respectively. It is well known that calculation of vibrational energy $U(T)$ for polyatomic solids such as mullites is difficult using a single Debye term in the quasi-harmonic approximation. The parabolic Debye phonon spectrum with a characteristic cut-off frequency cannot truly represent the PDOS. The calculated PDOSs of 2:1 and 3:2 mullites show more or less a single continuum (see later). Accordingly, a single Debye spectrum should represent each of the PDOS neglecting the Van Hove singularities. However, in some cases for better description, in particular for the axial negative thermal expansion, we extended the equation (1) [34] as follows, leading to two Debye terms associated with one for positive thermal expansion and the second one for negative thermal expansion.

$$M(T) = M_0 + \frac{\gamma_1}{K_0} U_{D1}(T) + \frac{\gamma_2}{K_0} U_{D2}(T) \quad (2)$$

Figure 6 depicts the excellent fit between the model line and the observed data for the metric parameters as well as the thermal expansion coefficients. The fitted parameters are given in table 4.

Table 4: Fitting constants of the metric parameters and the obtained elastic values.

2:1 mullite						
Metric	M_0	θ_{D1}/K	θ_{D2}/K	γ_1	γ_2	$s\gamma/10^{-3}$
a /pm	757.63(8)	1357(13)	399(4)	3.20(3)	-0.66(1)	2.20(1)
b /pm	768.29(13)	1100(18)	-	3.0(1)	-	11.39(1)
c /pm	288.54(3)	1196(13)	-	2.50(2)	-	4.26(1)
$V/\text{pm}^3 \cdot 10^6$	167.95(5)	1152(20)	406(7)	0.88(1)	-0.086(2)	17.85(1)
3:2 mullite						
a /pm	755.21(11)	1330(19)	417(6)	3.20(5)	-0.39(5)	2.72(1)
b /pm	769.19(11)	1101(16)	-	2.98(4)	-	11.07(1)

J. Am. Ceram. Soc.

<i>c</i> /pm	288.45(3)	1248(12)	-	2.49(3)	-	4.17(1)
<i>V</i> /pm ³ ·10 ⁶	167.56(5)	1287(36)	418(12)	0.83(2)	-0.01(1)	17.97(1)

γ_1 and γ_2 are Grüneisen parameter of the fitting Debye spectrum with the Debye temperature of θ_{D1} and θ_{D1} , respectively. For more details of the $s\gamma$, see text and equations (3 – 4) For cell volume, $s\gamma = s_a\gamma_a + s_b\gamma_b + s_c\gamma_c$

The integral term of the Debye function is numerically evaluated, and the bulk moduli (K_{VRH}) are taken from table 2 (polyfit for 3:2 and Ref. [16] for 2:1 mullite). A second Debye term was required to describe the *a*-cell parameter of both the 2:1 and 3:2 mullites, resulting in about a Debye frequency of $\sim 278 \text{ cm}^{-1}$ ($\sim 400 \text{ K}$) and $\sim 291 \text{ cm}^{-1}$ ($\sim 418 \text{ K}$) for 2:1 and 3:2 mullite, respectively. The axial negative Grüneisen parameter of this Debye spectrum in 2:1 mullite is almost two times greater than that of 3:2 mullite, which explains the more pronounced nature of the negative thermal expansion in 2:1 mullite than that in 3:2 mullite at low temperature. The contribution of the negative term is one order of magnitude higher in the bulk expansion (cell volume) of 2:1 mullite than that of the 3:2 mullite. The Debye temperatures of the *a*- and *b*-cell parameters are comparable. The Debye temperature along the *c*-direction of the 3:2 mullite is higher than that of the 2:1 mullite, which may be due to significantly lower $K_{0,c}$ of 3:2 mullite than that of 2:1 mullite. Beside slight negative contribution of the Grüneisen parameters in the *a*-direction for both mullites, the sum of the terms (elastic compliance multiplied by the axial Grüneisen parameter) at the right-hand side in the following expressions ultimately determines the sign of the TECs of an orthorhombic system [34, 36]:

$$\alpha_a = \frac{C_p}{V} (s_{11}\gamma_a + s_{12}\gamma_b + s_{13}\gamma_c) \quad (3a)$$

$$\alpha_b = \frac{C_p}{V} (s_{12}\gamma_a + s_{22}\gamma_b + s_{23}\gamma_c) \quad (3b)$$

$$\alpha_c = \frac{C_p}{V} (s_{13}\gamma_a + s_{23}\gamma_b + s_{33}\gamma_c) \quad (3c)$$

$$\begin{aligned} \alpha_V &= \frac{C_p}{V} \{ \gamma_a (s_{11} + s_{12} + s_{13}) + \gamma_b (s_{12} + s_{22} + s_{23}) + \gamma_c (s_{13} + s_{23} + s_{33}) \} \\ &= \frac{C_p}{V} (s_a \gamma_a + s_b \gamma_b + s_c \gamma_c) \quad (4) \end{aligned}$$

where s_a , s_b and s_c are linear compressibility in the **a**-, **b**- and **c**-direction, respectively. For the calculation of $s_a \gamma_a$ and $s_V \gamma_V$, the averaged value of two Grüneisen parameters was taken (Tab. 4). Since in all cases the $s\gamma$ term is positive (Tab. 4), the overall axial as well as the volume thermal expansions at ambient condition are positive.

3.3. Vibrational property

The Raman spectra and the PDOSs of 2:1 and 3:2 mullites are shown in figure 7. Due to structural relations the analogy of the vibrational features of sillimanite seems to be an ideal starting point for a better interpretation of the Raman spectra of mullites. Earlier Salje and Werneke [37] interpreted the Raman spectra of sillimanite. Mernagh and Liu [38] demonstrated pressure-dependent effects of some selective Raman bands, where two bands at 236 cm⁻¹ and 311 cm⁻¹ were observed with negative mode Grüneisen parameter. The irreducible representations corresponding to sillimanite at the Γ -point are: 13A_{1g} + 13B_{2g} + 8B_{2g} + 8B_{3g} + 11A_{1u} + 11B_{1u} + 16B_{2u} + 16B_{3u}, where 42 are Raman active (13A_{1g} + 13B_{2g} + 8B_{2g} + 8B_{3g}), 40 are infrared active (10B_{1u} + 15B_{2u} + 15B_{3u}) along with acoustic (B_{1u} + B_{2u} + B_{3u}), and 11 silent/optically inactive (11A_{1u}) modes. Al atoms in sillimanite located at an inversion center (4a) are not Raman active. Therefore the Raman spectrum of sillimanite comprises of the scattering from all other atoms associated with the regularly ordered AlO₄ and SiO₄ tetrahedra.

Figure 7: Phonon density of states calculated by GULP and Raman spectra obtained at ambient condition.

The tetrahedral linking O3-atom contributes to scattering with six modes ($2A_{1g} + 2B_{2g} + B_{2g} + B_{3g}$). These six modes are inactive in mullites as the O3-atom in mullite locates at the inversion center due to statistical distribution of AlO_4 and SiO_4 with an averaged Al/Si-O3 bond length. The presence of T_3O and T_4O clusters and the associated vacancies in mullite lead to a complicated vibrational feature as the spectral density is sensitive to vacancy and disordering [39]. Thus a straightforward group theory may not predict the accurate number of optically active modes in the Brillouin zone center. For instance, study on some binary oxides Michel et

al. [40] documented Raman spectra of some disordered phases showing broad bands, leading to breakdown of the selection rule ($k = 0$). Keramidas and White [39] interpreted the Raman spectrum of a calcia-stabilized zirconia (CSZ) by using inelastic neutron scattering (INS) on a single crystal of UO_2 . The Raman activity of CSZ was found in the same frequency range as shown by the INS spectrum of UO_2 . Moreover, the highest frequency observed by Raman corresponds to the highest frequencies of the INS spectrum. Instead of the unique T_{2g} mode of UO_2 at around 460 cm^{-1} , all modes become Raman active. That is, the random distribution of massive point defects suppresses the translational symmetry, leading to a breakdown of the selection rules, and phonons from all possible parts of the Brillouin zone contributed to the Raman spectrum. From the comparative view between sillimanite, 2:1 mullite and 3:2 mullite along with their respective PDOSs it is clear that the vibrational features (Fig. 7), in particular the broadening of the bands of the mullites is significantly different from those of sillimanite. The line broadening was explained by Michel et al. [41], McMillan et al. [42] and Rüscher [43] in terms of random occupation of Al- and Si-atoms on the T-sites. The possible tricluster and/or tetracluster and the vacancies are assumed to be discrete in population, thus are short-range ordered, results in loss of vibrational coherence as discussed above. Except the mid-range, each Raman spectrum with broad bands partly represents the respective PDOS, indicating a sort of breakdown of the selection rule. The mid-range of the Raman spectra can be resolved into broad bands, however with higher spectral intensity which is more pronounced in 2:1 mullite than in 3:2 mullite, indicating more vacancy/disordering in 2:1 mullites than those of 3:2 mullites. An *ad hoc*, however convenient, way is to study the hypothetical mullite with no vacancy ($x = 0$), which allows the crystal structure with fuller occupancy of all atoms in the asymmetric unit with an additional assumption of a statistical distribution of Al and Si on the T-site ($4h$) [41].

Accordingly, the irreducible representations decompose into the Γ -point as $6A_g + 5A_u + 6B_{1g} + 5B_{1u} + 3B_{2g} + 10B_{2u} + 3B_{3g} + 10B_{3u}$, where there are 18 ($6A_g + 6B_{1g} + 3B_{2g} + 3B_{3g}$) Raman active, 22 ($4B_{1u} + 9B_{2u} + 9B_{3u}$) IR active along with acoustic ($B_{1u} + B_{2u} + B_{3u}$) and 5 silent ($5A_u$) modes. As such the Raman spectrum collected at ambient condition requires 18 Pseudo-Voigt bands both for the 2:1 and 3:2 mullites.

The PDOS describes the vibrational properties of solids, which plays a crucial role in numerous microscopic as well as macroscopic phenomena such as thermodynamic phase-transitions, thermal expansion, optical absorption and Raman scattering. Selective low- and high-frequency regions of the PDOSs of 2:1 and 3:2 mullites are shown in figure 8.

Figure 8a: Temperature-dependent phonon density of states (PDOS) of 2:1 mullite obtained from GULP calculation.

Figure 8b: Temperature-dependent phonon density of states (PDOS) of 3:2 mullite obtained from GULP calculation.

The high-frequency region in both cases show usual quasi-harmonic behaviors. That is, the frequency decreases with increasing cell volume. However, the low-frequency region (e.g., model-4 of 2:1 mullite, and model-5 of 3:2 mullite, which are energetically the most stable phases) shows an opposite behavior. For instance, at around 160 cm^{-1} the spectral density of 2:1 mullite exhibits modes with negative Grüneisen parameters. The center of the region is shifted to

about 170 cm⁻¹ for the 3:2 mullite, however, modes of negative Grüneisen parameters are not that much pronounced as in 2:1 mullite. To further validate this feature thermal anharmonicity of Raman bands have been analyzed. Anharmonicity of the phonon involves phenomena beyond that of an independent (normal) phonon. The higher-order phonon-phonon interactions are the main source of the anharmonic behavior, which causes the frequency of a harmonic oscillator to be temperature dependent. The temperature dependency of the phonon frequency arises from two different sources: (i) a pure-volume effect associated with the thermal expansion (quasi-harmonic), and (ii) a pure-temperature effect that is present even at a constant volume (isochoric). The temperature-dependent Raman spectra of 2:1 and 3:2 mullites have been measured between 78 K and 500 K as shown in figure 9.

Table 5: Selective Raman frequencies at 0 K (ω_{i0}), their corresponding mode Grüneisen parameters (γ_i) together with the fitting damping parameters (A , B) used for Eq. (9).

2:1 mullite			
ω_{i0} /cm ⁻¹	$(\gamma_i)_T$	A /cm ⁻¹	B /cm ⁻¹
249.3	-0.31(2)	-	-
306	2.64(1)	-	-0.056(1)
415.5	3.31(2)	-1.81(1)	-
611.2	1.28(3)	-1.20(1)	-
710.9	3.12(8)	-3.82(2)	-
963.3	0.21(4)	-	-0.12(5)
1030	1.95(1)	-8.04(5)	-0.30(1)
1132	1.35(1)	-5.23(2)	-0.65(1)
3:2 mullite			
251.7	4.87(1)	-	-0.06(1)
308.1	6.44(9)	-0.83(2)	-0.072(1)
414.6	2.56(4)	-	-0.13(2)
602.2	2.83(5)	-	-0.44(1)
719.1	1.30(3)	-2.66(5)	-
962	1.20(5)	-	-0.96(3)

J. Am. Ceram. Soc.

1035	3.21(1)	-	-3.66(1)
1135	2.98(1)	-	-4.10(1)

Figure 9: Temperature-dependent Raman spectra of mullites. Temperature (78 K – 103 K, 113 K – 293 K, and 300 K– 500 K with step 5 K, 10 K and 20 K, respectively) increases in the direction of the arrow.

Due to broad features and possible compound nature of most bands selective phonon modes allowed for the anharmonicity analysis. At ambient condition the obtained band maxima are in good agreement with the reported ones [43]. The band positions at low temperatures are extrapolated (cubic polynomial with the second coefficient fixed to zero for physically meaningful $\partial\omega_i/\partial T \rightarrow 0$ at 0 K) down to 0 K as given in table 5. The mode-Grüneisen parameter was calculated from the volume derivative as:

$$\gamma_i = -\left(\frac{\partial \ln \omega_i}{\partial \ln V}\right) \quad (5)$$

The corresponding cell volumes were taken from the respective thermal expansion model fitting. The temperature-dependent frequency of a Raman phonon mode can be written according to the following expression:

$$\omega_i(T) = \omega_{i,0} + \Delta\omega_i(T) \quad (6)$$

where $\omega_{i,0}$ is the harmonic frequency and $\Delta\omega_i(T)$ refers to total frequency shift which can be expressed as an additive term of two contributions:

$$\Delta\omega_i(T) = \Delta\omega_i^{latt} + \Delta\omega_i^{anh}(T) \quad (7)$$

$\Delta\omega_i^{anh}(T)$ refers to the frequency shift due to phonon-phonon interactions (*Umklapp*); the term is also known as the pure temperature contribution. $\Delta\omega_i^{latt}(T)$ is the frequency shift due to volume

thermal expansion. Assuming that the temperature-dependent change of both K_0 and γ_i are negligible, the term $\Delta\omega_i^{latt}(T)$ can be expressed as:

$$\Delta\omega_i^{latt} = \omega_{i,0} \left[\exp \left\{ - \int_0^T \gamma_i \alpha_V(T) dT \right\} - 1 \right] \quad (8)$$

The observed $\Delta\omega_i^{anh}(T)$ can be modeled using modified Klemens approach [44, 45] considering the phonon decay into two channels namely, 3-phonon and 4-phonon interactions:

$$\Delta\omega_i^{anh}(T) = A \left[\frac{2}{\exp\left(\frac{hc\omega_{i0}}{2k_B T}\right) - 1} \right] + B \left[\frac{3}{\exp\left(\frac{hc\omega_{i0}}{3k_B T}\right) - 1} + \frac{3}{\left\{ \exp\left(\frac{hc\omega_{i0}}{3k_B T}\right) - 1 \right\}^2} \right] \quad (9)$$

A and B are damping factors (Tab. 5) representing the relative probability of the occurrences of the 3-phonon (cubic decay) and 4-phonon (quartic decay) processes contributing to the frequency shift, respectively. Despite the broad features of the bands the model well describes the observed data for the thermal anharmonicity of the 3:2 mullite as shown in figure 10, where the scattering of the data are not that much pronounced as those for the 2:1 mullite. Almost all of the modes smoothly soften, and $\Delta\omega_i^{anh}(T)$ mostly dominates over $\Delta\omega_i^{latt}(T)$ for the whole temperature range. In general, the observed spectral data appearing elsewhere above and below the model line demonstrate hardening and softening of the corresponding mode, respectively. The modes of 2:1 mullite appear below 1000 cm^{-1} hardly follow the applied model (symmetric decay) and cannot be modeled with reasonable satisfaction.

The positive anharmonicity values above the model line in particular at low temperatures indicate negative Grüneisen parameters of the associated modes, contributing to the contraction

of the cell volume with increasing temperature. As such the mode at $\sim 250\text{ cm}^{-1}$ shows positive anharmonicity for the whole temperature range. Modes at 1030 cm^{-1} and 1133 cm^{-1} are assigned to AlO_4 and SiO_4 related vibrations, respectively [42, 43]. Both they require higher damping factors for 2:1 mullite than those for the 3:2 mullite. The observed behaviors clearly hint for the thermal anharmonicity of the selective phonons to be more pronounced in 2:1 than in 3:2 mullite.

Figure 10: Temperature-dependent change of phonon frequencies of some representative Raman bands of 2:1 (top) and 3:2 (bottom) mullites.

It was also observed in the thermal behaviors of the PDOS in the low frequency region, and may be related to the corresponding negative Grüneisen parameters (Tab. 2) observed along the *a*-direction at low temperatures. The phonon spectral distribution is almost similar to the blackbody distribution of photons, and at low temperature the long-wavelength phonons mostly control the thermal behaviors of the solids, which are hardly impacted by defects such as vacancies in mullites. Therefore it may not be surprising that below a critical temperature the vacancies in mullites do not play any roles as scattering centers, leading to an irregular change of anharmonicity of the associated phonons.

4. Conclusion

Thermal behaviors of 2:1 and 3:2 mullites have been studied using X-ray and neutron powder diffractions, Raman spectroscopy and computation. The temperature-dependent metric parameters of the 2:1 and 3:2 mullites extracted from the microscopic model would provide a guideline for theoretical calculations for a wide range of temperature. Beside a single Debye characteristic frequency, a second Debye spectrum with a negative Grüneisen parameter was required to model the *a*-cell parameter to describe slight contraction of the cell at low temperatures. Temperature-dependent phonon density of states shows spectral region with negative mode Grüneisen parameters at lower frequency. Low frequency Raman bands were also observed with negative Grüneisen parameters. These observations leave clear microscopic hints for the thermal contraction of the 2:1 and 3:2 mullites at low-temperatures.

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J. Am. Ceram. Soc.

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