

MODELLING OF MULLITE SOLID-SOLUTIONS IN THE SYSTEM $\text{Al}_2\text{O}_3\text{-SiO}_2$

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(Received 5 January 2002; accepted 3 March 2002)

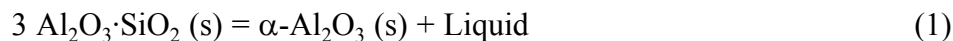
Abstract

A model for the mullite formation from kaolinites and the solid-solution range of mullite in the $\text{Al}_2\text{O}_3\text{-SiO}_2$ system has been evaluated. This rather complicated model implies that both octahedral and tetrahedral coordinated Al^{3+} -ions as well as tetrahedral Si^{4+} -ions participate together with O^{2-} ions and vacant oxygen positions during the rearrangements in the structure during the sintering process at high temperatures.

Keywords: mullite, $\text{Al}_2\text{O}_3\text{-SiO}_2$, solutions

1. Introduction

It is well known that mullite, $3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$, is the only compound formed between the compounds in the binary system $\text{Al}_2\text{O}_3\text{-SiO}_2$ at ordinary pressures (1 bar) and high temperatures. For many years there has been a continuous discussion whether mullite melts congruently or incongruently. Today it seems to be accepted that mullite melts incongruently at $\sim 1828^\circ\text{C}$ according to the equation:



The crystal structure of mullite has been interpreted for a long time as a modified defect structure of sillimanite, in which the mullite stoichiometry is achieved by substituting Si^{4+} -ions with Al^{3+} -ions in the tetrahedral sites of the alternating aluminium and silicon columns.

Holm and Kleppa [1] for instance suggested in 1966 that the mullite structure could be derived from the structure of sillimanite, $\text{Al}^{\text{VI}}[\text{Al}^{\text{IV}}\text{Si}]_5\text{O}_5$, by distributing the tetrahedrally coordinated aluminium and silicon atoms over

their formerly ordered positions as given by : $\text{Al}^{\text{VI}} \left[\text{Al}^{\text{IV}}_{\frac{1}{4}} \text{Si}^{\text{IV}}_{\frac{3}{4}} \right] \text{O}_{\frac{7}{8}}$

This model was also accepted and used by Aksay et al [2] in their work from 1991. They suggested the following scheme for the substitution in the lattice



and stated that in their model for the solid-solution in the system the octahedral AlO_6 clusters do not change during the rearrangements in the structure. They expressed the following defect structure model for the mullite composition:



However this model has recently been questioned by Holm [3,4]. His calculations show that the unit cell of sillimanite is not comparable in size with the unit cell of mullite.

From the formula given for mullite, $\text{Al}_{\frac{1}{2}} \text{Si}_{\frac{3}{4}} \text{O}_{\frac{7}{8}}$ which corresponds to a molecular weight of 159.77 g mol⁻¹, a density 3.17 g cm⁻³ and cell volume 167.35 Å³, the Z value can be calculated:

$$Z = \frac{\rho \cdot V \cdot N_A}{M} = 2 \text{ units} \quad (4)$$

As can be seen from Table 1, both structures are orthorhombic, but while the unit cell of sillimanite contains $4[\text{Al}_2\text{SiO}_5]$ units, the unit cell of mullite contains only $2\left[\text{Al}_{\frac{2\frac{1}{4}}{4}}\text{Si}_{\frac{3}{4}}\text{O}_{\frac{4\frac{7}{8}}{8}}\right]$ units.

Table 1: Cell parameters, volumes and densities for mullite and sillimanite

	a [Å]	b [Å]	c [Å]	V [Å ³]	Z	d [g cm ⁻³]	Ref.
Mullite	7.5456	7.6898	2.8842	167.35	0.75	3.170	PDF 15-0776
Sillimanite	7.486	7.675	5.7729	331.68	4	3.258	PDF 38-0471

In a paper by Holm [4] on the kaolinites-mullite transformation in the Al_2O_3 - SiO_2 system, gels of synthetic kaolinites formed from mixtures of very pure metalorganic compounds of aluminium and silicon and with seven different Al/Si ratios, were investigated by DTA/TG/DTG up to 1200°C. The enthalpies associated with the exothermic reaction occurring at 980°, were determined and plotted as a function of composition. The enthalpies obtained reached a maximum at a composition corresponding to $2\text{Al}_2\text{O}_3 \times 3 \text{SiO}_2$. The result was discussed with reference to the well known work by Brindley and Nakahira [5] from 1959 on the kaolinite-mullite reaction series. Good correlation between the experimental enthalpies and the enthalpies of crystallization of alumina and silica taken from the literature were obtained. Models for distribution of the Al-atoms between the octahedral and the tetrahedral positions in the mullite structure were discussed, and models for the incongruent melting of both 3:2 mullite and 2:1 mullite were also evaluated.

2. Results and Discussion

On the basis of the results referred in the introduction, the mullitization process and the formation of primary mullite will be discussed. A model for

the solid-solution formation in the system and the extent of the solid-solution range will also be discussed.

a) Al₄Si₃O₁₂ (“the spinel phase”)

The so-called “spinel phase” Al₄Si₃O₁₂ formed from kaolinite at 980°C will be the logical starting point for a discussion of the mullitization process. By further heating above 1000°C silica will be discarded from the spinel structure according to the equation:



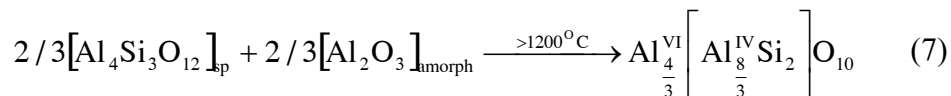
and the Al₄Si₂O₁₀-unit is formed. It is important to notice that this unit will be the basic unit for the formation of the different mullites in the Al₂O₃-SiO₂ system during further heating.

b) Al₄Si₂O₁₀ (1:1 composition)

As already shown by Holm [4] the Al₄Si₂O₁₀-unit can be considered to consist of two separate units given by:



By further heating the following reaction will take place

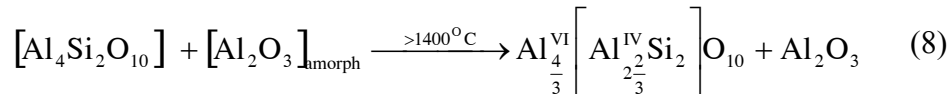


The Al-ions outside the spinel phase will during the sintering process enter the lattice in octahedral positions while the Al³⁺- and Si⁴⁺-ions in the spinel phase will remain in tetrahedral positions.

c) Al₆Si₂O₁₃ (3:2 mullite)

The formation of the 3:2 mullite which consists of the units Al₄Si₂O₁₀ +

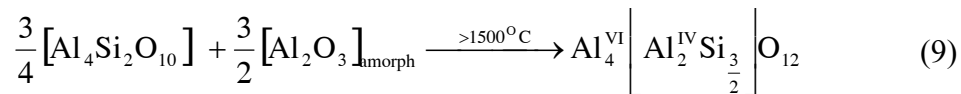
Al₂O₃ will start as follows:



which again will react during the sintring process at higher temperatures (T> 1400°C) to the final 3:2 mullite, as has been shown by Holm [4].

d) Al₆Si_{3/2}O₁₂ (2:1 mullite)

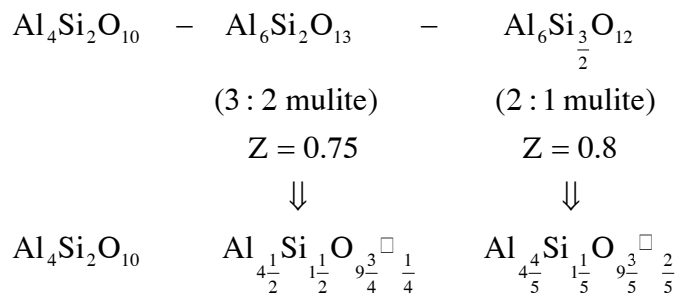
A corresponding scheme can be given for the formation of the so-called 2:1 mullite from the following units



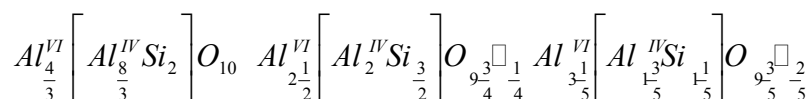
also here with a final distribution of the Al-ions for the 2:1 mullite in accordance with the distribution given in the paper by Holm [4].

e) Solid solution model for mullite

In the evaluation of a model for the solid solution between the three members in the system:



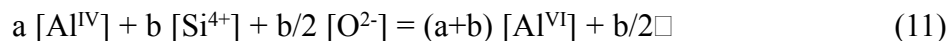
one has to look at the distribution of the Al-ions between octahedral and tetrahedral positions as has been done in the following three schemes for their unit cells:



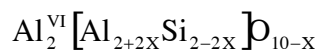
The following solid-solution model can now be evaluated on the basis of the distributions given above:



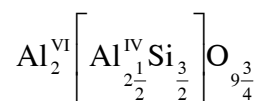
This model implies that the following substitutions occur between the members in the composition range 50 – 67 mol% Al₂O₃ in the system:



This is different from the model or scheme given in Eq. (3).



For the 3:2 mullite composition this model gives the following distribution:



compared to one given in this work:

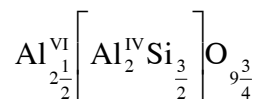


Table 2 give compositions, cell dimensions as well as calculated densities for seven members belonging to the solid solution series in the composition range 50-100 mol% Al_2O_3 . The distributions on octahedral and tetrahedral sites are calculated from Eq. (10). The cell dimensions are taken from the works of Cameron [6,7] for four of the members. For the 7:4 and 2:1 compositions the data are own determinations (see appendix).

Table 2. Compositions and cell dimensions of compounds in the solid solution series in the Al_2O_3 - SiO_2 system

Compound	Composi- tion mol% Al_2O_3	Ref.	Cell dimensions [\AA]			Volum [\AA^3]	d_{calc} g/cm ³	d_{meas} g/cm ³
			a	b	c			
1:1 $\text{Al}_4^{\text{VI}} \left[\text{Al}_2^{\text{IV}} \text{Si}_2 \right] \text{O}_{10}$	50	6	7.554	7.69	2.884	167.31	3.22	
3:2 $\text{Al}_{\frac{3}{2}}^{\text{VI}} \left[\text{Al}_2^{\text{IV}} \text{Si}_{\frac{1}{2}} \right] \text{O}_{\frac{9}{2} \square_{\frac{1}{4}}}$	60	6	7.548	7.693	2.884	167.47	3.168	
7:4 $\text{Al}_3^{\text{VI}} \left[\text{Al}_{\frac{2}{3}}^{\text{IV}} \text{Si}_{\frac{1}{3}} \right] \text{O}_{\frac{7}{3} \square_{\frac{1}{3}}}$	63.6	This work	7.576	7.688	2.888	168.20	3.137	3.14
2:1 $\text{Al}_{\frac{2}{5}}^{\text{VI}} \left[\text{Al}_{\frac{1}{5}}^{\text{IV}} \text{Si}_{\frac{1}{5}} \right] \text{O}_{\frac{3}{5} \square_{\frac{2}{5}}}$	66.7	This work	7.585	7.694	2.886	168.40	3.123	3.13
5:2 $\text{Al}_{\frac{5}{3}}^{\text{VI}} \left[\text{Al}_{\frac{1}{3}}^{\text{IV}} \text{Si}_{\frac{1}{3}} \right] \text{O}_{\frac{7}{2} \square_{\frac{1}{2}}}$	71.4	6	7.604	7.68	2.892	168.90	3.09	
4:1 $\text{Al}_{\frac{4}{3}}^{\text{VI}} \left[\text{Al}_{\frac{1}{3}}^{\text{IV}} \text{Si}_{\frac{1}{3}} \right] \text{O}_{\frac{7}{3} \square_{\frac{1}{3}}}$	80	6	7.66	7.66	2.90	170.15	3.04	
$\text{Al}_6^{\text{VI}} \left[\right] \text{O}_9 \square_{1,0}$	100	This work	7.69	7.69	2.905	171.80	2.956	

*This work, extrapolated cell dimensions from Cameron [6]

The densities are plotted as a function of n_{vacancy} in Fig. 1. As can be seen the calculated densities fit nicely to a straight line. The density obtained by extrapolation to $n_{\text{vacancy}} = 1$ is 2.93 g/cm³.

The end member, $\text{Al}_6^{\text{VI}} \left[\right] \text{O}_9 \square_{1,0}$ corresponds to a mullite-type silica free aluminate, and has been discussed in the literature before by Foster [8] in 1959 and by Perrotta and Young [9] in 1974. Their data are given in Table 3 together with our own calculated d-values based on a tetragonal cell with lattice constants $a = b = 7.69 \text{ \AA}$ and $c = 2.905 \text{ \AA}$, again taken from the work by Cameron [6].

Table 3. X-Ray diffraction data for mullite-type aluminate ($m\text{-Al}_2\text{O}_3$)
($a = b = 7.69 \text{ \AA}$, $c = 2.905 \text{ \AA}$)

hkl	$\tau\text{-Al}_2\text{O}_3^*$		$m\text{-Al}_2\text{O}_3^{**}$	
	d_{calc}	d_{meas}	d_{meas}	I/I_0
110	5.44	5.45	5.34	89
120	3.44	3.47	3.40	100
001	2.91	2.92	2.89	33
220	2.72	2.72	2.69	81
111	2.56	2.59	2.55	70
201	2.32	2.34	2.31	25
121	2.22	2.24	2.21	56
230	2.13	2.15	2.11	44
221	1.99	1.99		
140	1.87	1.88	1.86	19
240	1.72	1.73	1.71	26
041	1.60	1.61	1.60	17
411	1.57	1.55	1.53	41
510	1.50	1.492	1.475	16
421	1.48	1.461	1.453	23
520	1.43	1.41	1.419	9
440	1.36	1.346	1.358	7

* Ref. (8)

** Ref. (9)

The density calculated on the basis of this cell is 2.956 g/cm^3 . This value should be compared with the extrapolated value in Fig.1. (2.93 g/cm^3). This good agreement can be taken as a strong support for the X-ray data given by Cameron [6], as well as for the model for the solid solution series for mullite in the $\text{Al}_2\text{O}_3\text{-SiO}_2$ system as given in Eq. (10) in this work.

APPENDIX: X-ray investigation of fused mulite from Keith Ceramics, England:

Chemical Analysis: $72.9 \text{ w \% Al}_2\text{O}_3$
 24.9 w \% SiO_2

Corrected: $74.1 \text{ w \% Al}_2\text{O}_3$

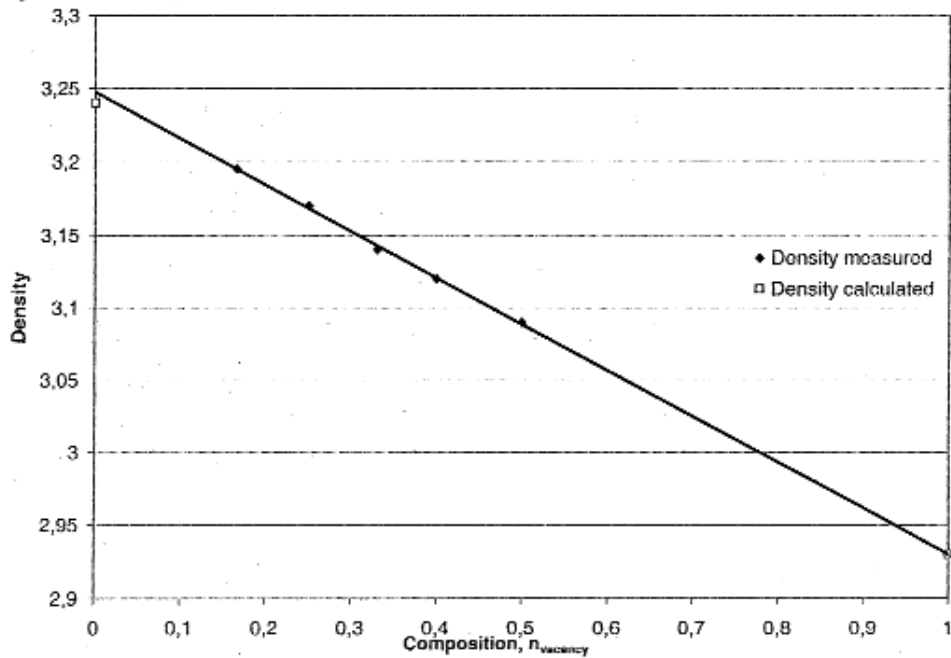


Fig.1. Densities of $Al_2O_3+SiO_2$ mixtures as a function of composition

Mole %: 62.5 % Al_2O_3 + 37.5 % SiO_2 corresponding to $7/3 Al_2O_3 \cdot 4/3 SiO_2$
 $= Al_{14/3}Si_{4/3}O_{29/3}$

Unit Cell: $Al_{14/3}Si_{4/3}O_{29/3}$, $a = 7.576 \text{ \AA}$, $b = 7.688 \text{ \AA}$, $c = 2.888 \text{ \AA}$

$d_{\text{calculated}} = 3.137 \text{ g/cm}^3$

$d_{\text{measured}} = 3.14 \text{ g/cm}^3$

The results from the X-ray investigation are given in Table 4.

Table 4. Results from X-ray examination of Keith ceramics fused mullite.
($d_{\text{calculated}}$: $a = 7.576 \text{ \AA}$, $b = 7.688 \text{ \AA}$, $c = 2.888 \text{ \AA}$)

hkl	$d_{\text{calculated}}$	d_{measured}	I %
110	5.3995	5.3933	66
200	3.7878	3.7866	2
120	3.4280	3.4247	91
210	3.3981	3.3995	92
001	2.8880	2.8864	26
220	2.6978	2.6990	62
111	2.5466	2.5448	85
130	2.4275	2.4271	47
310	2.3994	2.3824	2
021	2.3088		
201	2.2966	2.2966	25
121	2.2086	2.2078	100
230	2.1224	2.1223	67
320	2.1105	2.1055	1
221	1.9714		
040	1.9220	1.9210	6
400	1.8939	1.8953	6
140	1.8631	1.8627	5
311	1.8455	1.8459	15
330	1.7987	1.7987	2
240	1.7140	1.7142	27
321	1.7040	1.7003	33
420	1.6988		
041	1.6001	1.5992	8
401	1.5837	1.5847	3
141	1.5656	1.5646	1
411	1.5512	1.5526	62
331	1.5267	1.5268	2
150	1.5069	1.5062	2
510	1.4866		
241	1.4739	1.4733	11
421	1.4643	1.4650	21
002	1.4481	1.4433	12
250	1.4247	1.4242	12
520	1.4096	1.4069	8
112	1.3950	1.3943	3
202	1.3493	1.3497	5
440	1.3490		

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