JOURNAL OF MATERIALS SCIENCE **36** (2001) 5403–5406

High-temperature X-ray diffraction analysis of a low-fusing dental ceramic

S. ASSMANN
Degussa Dental GmbH & Co. KG, Rodheimer Straße 7, D-61191 Rosbach, Germany

M. ERMRICH*
X-ray Laboratory Dr. Ermrich, Am Kandelborn 7, D-64354 Reinheim, Germany
E-mail: roentgenlabor-dr.ermrich@t-online.de

K. KUNZMANN
INFRACOR GmbH, P.O. Box 1345, D-63403 Hanau, Germany

In the present study, the leucite growth of a low-fusing dental ceramic has been investigated by high temperature X-ray diffraction analysis. The process involved two heating and cooling cycles, starting with a totally amorphous powder. Maximum leucite growth has been detected via intensity and FWHM (Full Width at the Half Maximum) analysis of the X-ray reflections at a temperature of approximately 670°C upon cooling the sample, thus indicating a maximum CTE (Coefficient of Thermal Expansion) 110°C below the recommended firing temperature of the sample. © *2001 Kluwer Academic Publishers*

1. Introduction

Since the basic development of Weinstein *et al.* in 1962 [1, 2], dental ceramics can generally be fused to various metal alloys. The CTE of these materials heavily depends on the content of leucite ($KAlSi_2O_6$), that has been identified by many authors as the main crystalline phase in the standard dental porcelain [3–7]. High temperature X-ray examinations of the Component No. 1 of the Weinstein patent [1, 2] revealed a $CTE_{25-400^\circ C}$ of tetragonal leucite (low-temperature-form) close to $22.3 \times 10^{-6}/^\circ C$ [4] in contrast to the low $CTE_{25-400^\circ C}$ of $8.4 \times 10^{-6}/^\circ C$ corresponding to the glass matrix [4]. According to Mackert *et al.* [4] a martensitic transformation takes place in the Component No. 1 of the Weinstein patent above 400°C and the cubic (high-temperature) modification of leucite forms with a $CTE_{400-700^\circ C}$ of $21.5 \times 10^{-6}/^\circ C$. The phase change is also accompanied by a volume increase of the unit cell [4].

The prerequisite of leucite to form in dental porcelain is the location of its composition within the leucite precipitation field of the corresponding phase diagram [6]. In accordance with theory, tetragonal leucite was found to be a metastable phase at room temperature, that can be transformed into the thermodynamically more stable sanidine form by intensive heat treatment [8]. Upon further heating, the whole amorphous phase should theoretically be transformed into crystals, eventually forming feldspar, quartz and potassium tetrasilicate [6]. However, these stable final products from a thermodynamic point of view can generally not be detected in glass ceramics because of kinetic reasons [6, 8].

It is well known that the CTE of common (high fusing) dental ceramics changes with multiple firings or isothermal heat treatments [9–11]. This behaviour can be attributed to the growth (increase of CTE) or dissolving (decrease of CTE) of tetragonal leucite [9–11] within the glass matrix. When the tetragonal leucite with its high CTE is subsequently transformed into the thermodynamic more stable sanidine with a $CTE_{20-700^\circ C}$ of only 4–8 $\times 10^{-6}/^\circ C$ [8], the CTE of the overall glass-ceramic also decreases irreversibly with multiple firings [8].

The purpose of the present paper is to investigate leucite growth in a low-fusing porcelain supplied in an amorphous form by the manufacturer [12]. After the first temperature treatment, the change of the tetragonal leucite content (correlated to the intensity of the strongest diffraction peak) when heating the material for a second time will also be monitored, thereby simulating the first dentine bake. It is of special interest to determine the temperature at which the cubic leucite forms, when the maximum leucite growth occurs, at which temperature the leucite dissolves and if sanidine forms in the glass ceramic. With this information in mind, it should be possible to raise and lower the CTE of the porcelain by carefully controlling the firing parameters. Tensile or compressive stresses that sometimes form in the dental restauration can thus be closed, as they are related to a CTE mismatch between glass-ceramic and metal frame [13].

---

*Author to whom all correspondence should be addressed.

0022–2461 © *2001 Kluwer Academic Publishers*

2. Experimental procedures

The initially used low-fusing dental material has been supplied by the manufacturer [12] in an amorphous state, representing an intermediate stage in the production process. The dental ceramic is characterised by the following approximate composition (wt%):

SiO_2	60–70	Y_2O_3	0–0.2
Al_2O_3	10–15	SnO_2	0–1.0
K_2O	10–15	F	0–0.2
Na_2O	10–15	B_2O_3	0–1.0
CaO	0.0–0.2	CeO_2	0–1.0
BaO	0.0–0.2		

The X-ray investigations were carried out using the STOE θ/θ- diffractometer, Cu- K_α- radiation (U = 40 kV, I = 35 mA), a secondary beam monochromator and a scintillation counter. The high temperature attachment HDK-S1 (Johanna Otto GmbH) was used for the high temperature measurements. Therefore the powder was filled into an AlN- ceramic sample holder, which was directly heated by a platinum/rhodium ribbon. The experiment was completely controlled by a software package and the REP1800/Eurotherm 902P control unit. Table I shows the whole procedure, corresponding to Figs 1 and 2. The measuring time per diagram was about 6 min (region: $2\theta = 23$–$28°$, steps $\Delta 2\theta = 0.05°$, time per step $t = 2.5$ s). The upper limit of the applied temperature (820°C) exceeds the temperature of the first dentine bake claimed by the manufacturer [12] by approximately 40°C. When cooling down, the change of the leucite content was investigated in detail at 720°C (holding time of 60 min including two measurements, see Table I). This temperature is generally considered to coincide with the maximum leucite growth, thus raising the thermal expansion coefficient to higher values [12].

TABLE I Temperature regime of the high temperature measurements

Step	Mode	Temp. °C	Rate K/min	Wait t/min	T (Avg) °C	Measured file no.
1	Ramp	320	50.0			
2	Hold	320		0	320.0	1
3	Ramp	420	50.0			
4	Hold	420		0	420.1	2
5	Ramp	520	50.0			
6	Hold	520		0	520.0	3
7	Ramp	620	50.0			
8	Hold	620		0	620.0	4
9	Ramp	670	50.0			
10	Hold	670		0	670.0	5
11	Ramp	720	50.0			
12	Hold	720		0	720.0	6
13	Ramp	770	50.0			
14	Hold	770		0	770.1	7
15	Ramp	820	50.0			
16	Hold	820		0	820.0	8
17	Hold	820		4	820.0	
18	Hold	820		0	820.0	9
19	Ramp	770	50.0			
20	Hold	770		0	770.0	10
21	Ramp	720	50.0			
22	Hold	720		0	720.0	11
23	Hold	720		48	720.0	
24	Hold	720		0	720.0	12
25	Ramp	670	50.0			
26	Hold	670		0	670.0	13
27	Ramp	620	50.0			
28	Hold	620		0	620.0	14
29	Ramp	520	50.0			
30	Hold	520		0	520.0	15
31	Ramp	420	50.0			
32	Hold	420		0	420.0	16
33	Ramp	320	50.0			
34	Hold	320		0	320.0	17
35	Ramp	30	100.0			

TABLE II Crystallographic data of the leucite phases as given by the International Centre for Diffraction Data (ICDD) in the Powder Diffraction File (PDF) and the detectable lines in the observed angle region 2θ (see Fig. 1)

	$KAlSi_2O_6$	$KAlSi_2O_6$
PDF #	31 - 0967 high temp. form	38 - 1423
Lattice/space group	cubic, Ia3d	tetragonal, I41/a
	$a = 13.43(1)$ Å	$a = 13.0654(7)$ Å
		$c = 13.7554(13)$ Å
	$V_{red} = 1211.15$ $Å^3$	$V_{red} = 1174.06$ $Å^3$
Observed region 23–28° (2θ):		
Diffraction angle (2θ), hkl		25.383° (321)
		25.892° (004)
	26.531° (400)	
		27.277° (400)

The first experiment starts with the amorphous material. In a second experiment this crystallised material was heated again. The given temperature regime (see Table I) was used in both cases. The actual temperatures in Figs 1 and 2 correspond to the given file numbers. The detected peaks of leucite were matched using the crystallographic data listed in Table II.

3. Result and discussion

The 3D graphic Fig. 1 demonstrates the whole temperature process of the formation of the leucite phases: Starting the experiment using amorphous material at room temperature, a first idea of crystallisation is signed between 420°C and 520°C. Observing the (400)-reflection, the strongest line of the cubic leucite, the significant high temperature leucite phase formation starts at about 620°C. The further formation undergoes a local minimum at about 820°C. The maximum growth of cubic leucite then is reached at about 670°C to 620°C, during the described cooling process. At about 520°C the (400)- reflection is split into the two tetragonal reflections (004) and (400). The transition into the tetragonal phase is finished at about 320°C, accompanied by the visible formation of the (321) reflection. Measured at room temperature, only the tetragonal leucite is to be seen.

Starting with this material Fig. 2 demonstrates that the formation of the high temperature cubic leucite phase occurs now at 520°C. Here the reflections (004) and (400) of the tetragonal phase integrate into the (400) reflection of the cubic phase, the process is finished at about 620°C. The intensity of the (400) reflection again undergoes a minimum at 820°C. After the growth maximum of the cubic phase during cooling process in the

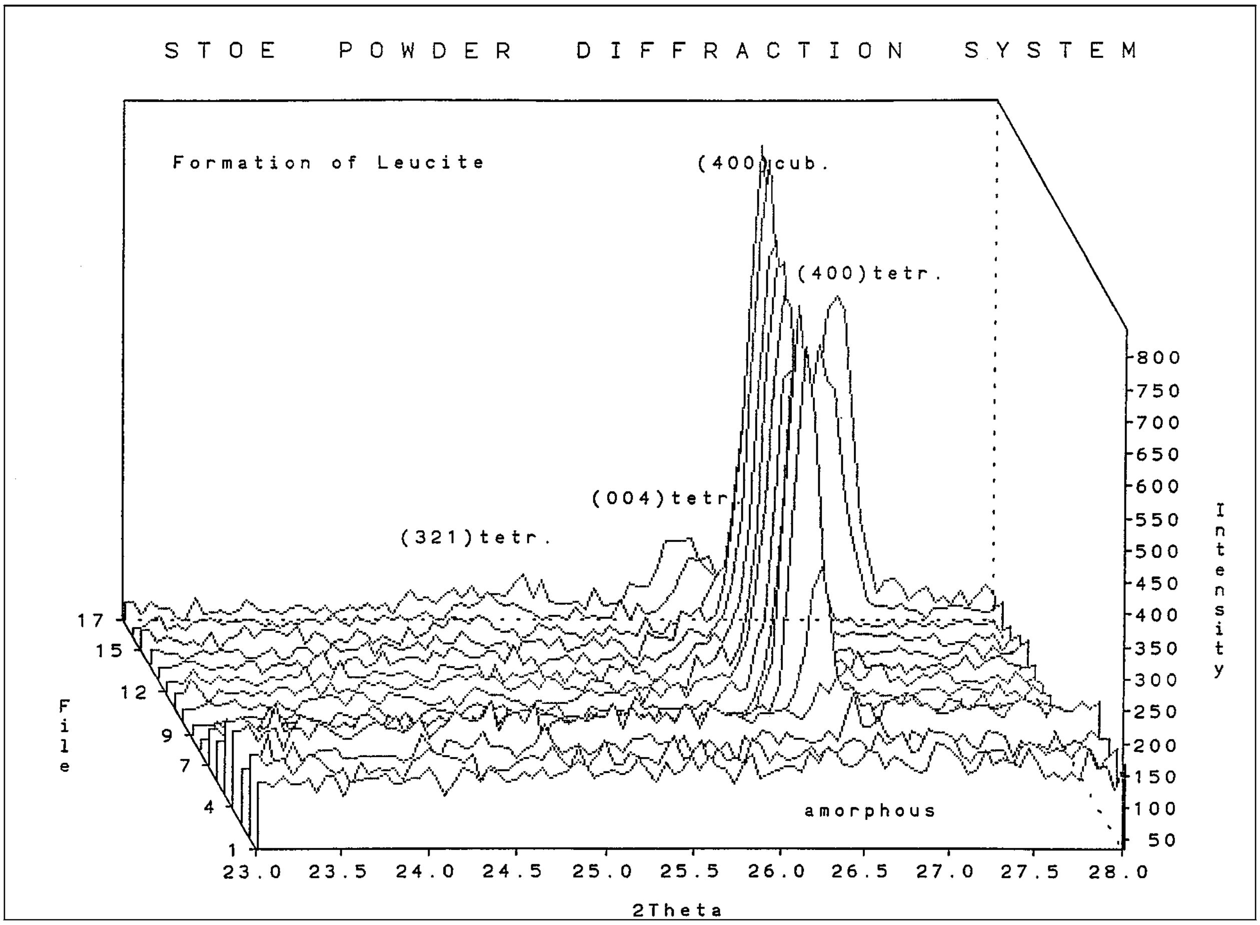

Figure 1 Experiment 1. Formation of the leucite phase, starting with amorphous material. Temperatures correspond to file numbers of Table I.

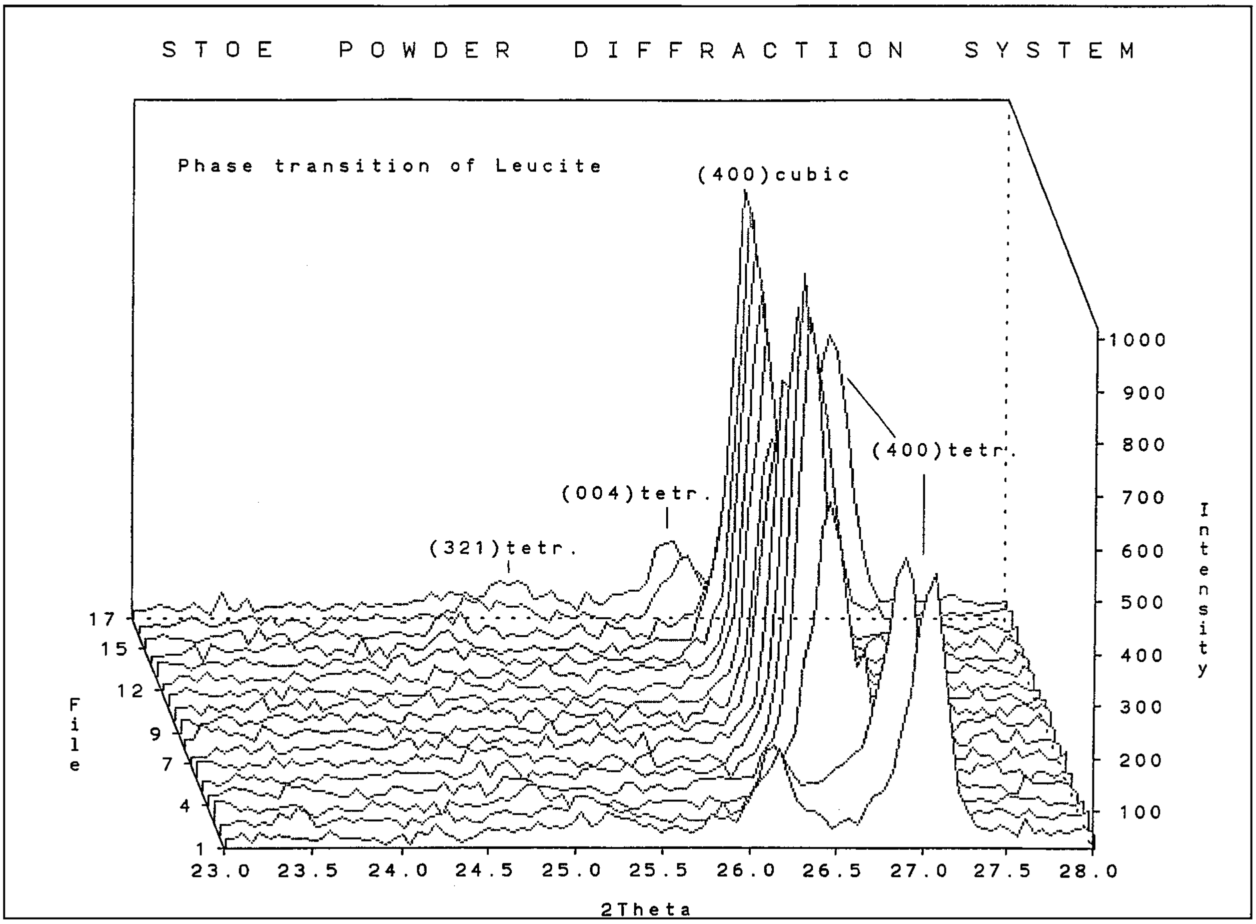

Figure 2 Experiment 2. Phase transition of the leucite, starting with crystallised material. Temperatures correspond to file numbers of Table I.

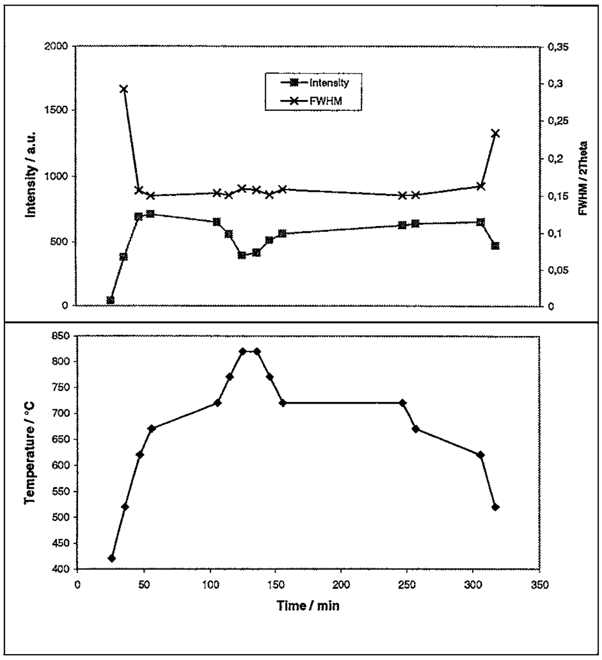

Figure 3 Maximum intensity as well as the FWHM (Full Width at Half Maximum) of the strongest observed leucite reflection (400) of the cubic phase in dependence on temperature, for the second experiment.

region of 720°C to 620°C the tetragonal phase is formed, which is again finished at about 320°C and completely stabilised up to room temperature.

Fig. 3 shows the maximum intensity as well as the FWHM (Full Width at Half Maximum) of the strongest observed leucite reflection (400) of the cubic phase in dependence on temperature, for the second experiment. The maximum intensity of the strongest leucite line corresponds to the maximum of leucite growth. It is not given at the highest temperatures, but during cooling in the temperature region of 670°C–620°C. The intensity of the reflection (400) undergoes even a local minimum, when the temperature of $T = 820°\text{C}$ is reached. Generally, the FWHM's indicate the quality of a lattice formation, smaller values point to a well crystallised lattice. So the higher values of FWHM indicate the formation process of cubic leucite during heating and to the retransformation into the tetragonal phase during cooling. The behaviour of the FWHM of the (400) reflection has got two minima corresponding to the maxima of cubic leucite content, but, also at 720 to 670°C during cooling, which agrees with the maximum of the measured intensity in this temperature region. That means finally, that the optimal crystallisation of the cubic leucite occurs at about 670°C.

The phases sanidine and orthoclase were not observed during both experiments, neither after starting with amorphous material nor after starting with partly crystallised tetragonal leucite.

4. Conclusions

To properly adjust the CTE of the ceramic in relation to the veneered alloy, according to the manufacturer the porcelain must be fired with a slow cooling cycle at the first dentine bake [12]. The experiment clearly documented the dependence of the leucite content on the applied temperature. Maximum leucite growth (and thus maximum CTE) occurs upon cooling around 670°C. Therefore, to meet the manufacturer requirements, the dental furnace of the technician must be carefully calibrated to avoid the occurrence of pressure stress cracks (caused by a low CTE and thus leucite content of the ceramic).

References

1. M. WEINSTEIN, S. KATZ and A. B. WEINSTEIN, US patent no. 3,052,982 (September 11, 1962).
2. M. WEINSTEIN and A. B. WEINSTEIN, US patent no. 3,052,983 (September 11, 1962).
3. C. HAHN and K. TEUCHERT, *Ceramic Forum Int. Ber. Dt. Keram. Ges.* **57** (1980) 208.
4. J. R. MACKERT JR., M. B. BUTTS and C. W. FAIRHURST, *Dent. Mater.* **2** (1986) 32.
5. J. R. MACKERT JR., M. B. BUTTS, R. MORENA and C. W. FAIRHURST, *J. Amer. Ceram. Soc.* **69** (1986) C.69.
6. M. M. BARREIRO, O. RIESGO and E. E. VICENTE, *Dent. Mater.* **5** (1989) 51.
7. P. W. PICHE, W. J. O'BRIAN, C. L. GROH and K. M. BOENKE, *J. Biomed. Mater. Res.* **28** (1994) 603.
8. M. M. BARREIRO and E. E. VICENTE, *J. Mater. Science: Mater. in Med.* **4** (1993) 431.
9. J. R. MACKERT, JR. and A. L. EVANS, *J. Dent. Res.* **70**(2) (1991) 137.
10. J. R. MACKERT, JR., S. W. TWIGGS and A. L. EVANS-WILLIAMS, *ibid.* **74**(6) (1995) 1259.
11. J. R. MACKERT, JR. and A. L. EVANS, *J. Amer. Ceram. Soc.* **74**(2) (1991) 450.
12. O. KOMMA, "Hydrothermale Dentalkeramiksysteme" (Ducera Dental GmbH&Co.KG, 1993).
13. S. ASSMANN, M. ERMRICH and K. KUNZMANN, *J. Mater. Science: Mater. in Med.* **12** (2000) 833.

Received 20 September 2000
and accepted 3 August 2001