Quantitative XRD Analysis of Hydrothermally-derived Leucite Content in Dental Porcelain Ceramics

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In this study, the leucite contents in the sintered porcelain and hydrothermally-derived powders were determined by the quantitative XRD analysis using internal standard. The leucite powders were prepared at 800 °C-1200 °C. The dental porcelain was sintered at 850 °C from the mixture of 20 mass% leucite prepared at 1100 °C and 80 mass% low temperature frit. The four standards for quantitative XRD analysis were established by mixing the low temperature frit (as a balance material), the copper (as an internal standard) and different weight content of pure leucite synthesized by molten method. They were X-rayed over the 2θ ranges from 14.5° to 17.5°, 26.5° to 28.5° and 42.5° to 44.5° for measuring the integrated area of leucite (211), (400) peaks and copper (111) peak. The area of leucite (211) and (400) peaks was divided by the area of copper (111) peak respectively and two calibration curves were plotted from these data. Before measuring the leucite content in the synthetic leucite, 40 mass% synthetic leucite was mixed with 60 mass% frit, whereas the leucite content in the sintered porcelain was determined by the method directly. The result of quantitative XRD analysis showed that the leucite content in the synthesized powders and dental porcelain correlated very well with the treating temperature and image analysis of SEM picture. The standards set in the study may be useful for measuring the leucite content in other systems.

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1. Introduction

Dental ceramics used for Porcelain-Fused-to-Metal (PFM) and all ceramic restorations are popular in dentistry for the time being.1 Leucite crystal, an important component of dental ceramics, possesses high coefficient of thermal expansion (CTE). It can reinforce dental porcelain and boost the CTE of dental materials to match that of metal substrate. Usually, leucite is introduced into dental porcelain by incongruent crystallization from feldspar or by synthetic leucite in powdered form.2-3 Traditional potash-feldspar-derived leucite is synthesized above 1150 °C with a liquid rich in SiO2.4-9 Thiel10 and Hashimoto11 investigated the leucite precursor was obtained from potash feldspar, and Bedard12 adopted analcime as a raw material to synthesize leucite. Ota13 obtained leucite from activated Al2O3, K2CO3 and SiO2 at 1200 °C. Chemical method has advantages in the fabrication of high purity materials with fine particle size at low temperature.10,11 Silica sol is a common raw material to introduce silicon source in chemical synthesis of inorganic material. For leucite synthesis, Liu12 and Erbe13 used silica sol to synthesize leucite powders by sol-gel method and Novatna14 synthesized leucite powders by hydrothermal method from silica sol. Though leucite powders have been synthesized by many methods, the relation between leucite content and treating temperature has not been determined yet.

Leucite content has a dramatic effect on the mechanical properties of the dental porcelain. Cesari15 investigated the effect of leucite content on the fracture toughness of dental porcelain and reported that there was an approximate positive linear relation between them. He concluded that the main toughening mechanism observed was crack deflection around leucite particles and clusters. Demry16 found that the addition of tetragonal leucite to dental porcelain could increase its flexural strength. Kon17 also reported that the strength of soda-lime glass matrix was enhanced along with the increasing of leucite content. Therefore, determining the leucite content in dental porcelain before comparing them is important and instructive for the research.

Quantitative XRD is a useful nondestructive analysis method to determine the crystalline content in materials,17 which has been adopted to facilitate the studies on kinetics and reaction mechanism.18 In this study, the leucite precursor was prepared by hydrothermal method and it was heat treated at different temperatures, and then the quantitative XRD method was utilized to analyze the leucite content in the obtained powders as well as in the prepared dental porcelain.

2. Materials and methods

The starting materials of low temperature frit, nona-hydrate aluminum nitrate (Al(NO3)3·9H2O), potassium nitrate (KNO3), nitric acid, urea, copper and Silica sol (30 mass% SiO2) were all purchased from Guangzhou Chemical Reagent Corporation. All the solvents and reagents were analytical grade except for Silica sol.

2.1 Synthesis of leucite

The preparation process of leucite has been introduced before.19-21 Specifically, silica sol, Al(NO3)3·9H2O and KNO3 were used as starting materials. At first, nitric acid was added into silica sol dropwise under strong stirring until the pH value of the solution reached 1-2. Then, the solutions of aluminum nitrate and potassium nitrate were mixed with the acidified silica sol in the K/Al/Si ratio of 1:1:2, which is the stoichiometric ratio of leucite. After urea (the urea/Al(NO3)3 ratio is 2:1) and an essential amount of de-ionized water were added into the K–Al–Si sol system, the sol was moved into a Teflon autoclave. The hydrolysis reaction took place statically at 200 °C in the autoclave for 3 h. After full hydrolysis reaction, the dense cake was collected and then dried at 100°C for 24 h. The acquired leucite precursor was ball-milled to pass 200 mesh sieve and then heat treated (SSJ-14A, Luoyang Shenzia Kiln Co., Ltd., China) under the rate of 600°C/h.
from room temperature to 300°C, 650°C, 750°C, 800°C, 850°C, 900°C, 1000°C, 1100°C, 1200°C respectively and was soaked for an hour before being cooled in the oven to room temperature. The obtained powders were labeled as L_{300}, L_{650}, L_{750}, L_{800}, L_{900}, L_{1000}, L_{1100} and L_{1200} respectively.

2.2 Fabrication of low temperature frit and dental porcelain

The starting materials of low temperature frit were SiO_{2}, Al_{2}O_{3}, K_{2}CO_{3}, Na_{2}CO_{3}, CaCO_{3}, CeO_{2}, Li_{2}O, CaF_{2}, MgO, BaCO_{3} and ZrO_{2}. They were mixed in a certain proportion and melted in an electric furnace at 1400°C for 1 h. A platinum crucible was used to avoid contamination of the frit. The melting frit was quenched in deionized water and was ball-milled (QM 2SP 20 Nanjing University Instrument Plant, China) to pass 200 mesh sieve. After drying, the frit had the following composition (mass%): 59% SiO_{2}, 13% Al_{2}O_{3}, 9% K_{2}O, 10% Na_{2}O, 2% CaO, 2% CeO_{2}, 1.5% Li_{2}O, 1% CaF_{2}, 1% MgO, 1% BaO and 0.5% ZrO_{2}. A mixture of 20 mass% L_{1100} and 80 mass% low fusing temperature frit was ball-milled in ethanol for 1 h and it was dry-pressed under 70 MPa to form a rectangular bar by a metal mold. The bar was heated to 850°C at 60°C/min and soaked at the temperature for 5 min in an electric furnace (Dentsply Multimat Touch, Germany), which was tagged as P_{1100}.

2.3 Sample characterization

The crystalline phases were determined by X-ray diffractometer (PANalytical X'pert PRO, Netherlands) from 10 (2θ) degree to 50 (2θ) degree, using Cu Kα radiation. The morphology of the samples was observed using scanning electron microscopy (LEO 1530 VP, Germany) under EM imaging. The SEM pictures were analyzed by image-analysis software (Image Pro Plus).

2.4 Method for quantitative XRD analysis

The leucite content in specimens was determined by quantitative X-ray diffraction technique, which was similar to that of Rasmussen. The pure leucite was prepared by the salt bath method reported by Oishi. After being milled and passing 200 mesh sieve, the pure leucite powders were mixed with the low fusing temperature frit in different weight fraction. The leucite content was 10, 20, 30 and 40 mass% respectively. Then, 10 mass% copper (internal standard) was added to these mixtures and they were labeled as S_{1}, S_{2}, S_{3} and S_{4}. They were X-rayed over the 2θ range from 14.5° to 17.5°, 26.5° to 28.5° and 42.5° to 44.5° for measuring the integrated intensity of leucite (211), (400) peaks and copper (111) peak. The scanning was carried out with the divergence slit size of 0.5°, step size of 0.002° and a count time of 30s. For each peak area measurement, five independent samples were recorded.

3. Results and discussion

Figure 1 shows the X-ray diffraction patterns for the dried leucite precursor, L_{300}, L_{650}, L_{750}, L_{800}, L_{900}, L_{1000}, L_{1100} and L_{1200} respectively. According to the XRD analysis, there were two phases in the dried leucite precursor, the amorphous phase (corresponding to the broad band on curve a, Fig. 1) and boehmite (the several small diffraction peaks on curve a, Fig. 1). When the precursor was treated at 300°C, KNO_{3} crystallized from the precursor as the major crystalline phase, while boehmite still existed at this temperature. Both L_{650} and L_{750} consisted of amorphous glassy phase only. Small amount of tetragonal leucite and kalsilite crystallized at 800°C (curve e of L_{900}, Fig. 1). On the upper-right corner, the detailed drawing of curve e clearly shows kalsilite (101) peak and (102) peak at 22.35 2θdegree and 28.62 2θdegree respectively. Kalsilite was the major crystalline phase at this temperature. With a small amount of kalsilite, there were two major solid phases in L_{450}, an amorphous component and tetragonal leucite. After being treated at 900–1200°C, leucite continued to crystallize from the precursor with the increasing of treating temperature, whereas kalsilite disappeared.

Surveying Fig. 1, the diffraction peaks of leucite increase with the increasing of the treating temperature and the (102) peak of kalsilite appears only on curve e and f. It has been reported that kalsilite is a metastable transition phase during the leucite crystallization process. Because the strong peaks of kalsilite do not overlap with that of leucite, the existence of kalsilite in the measured powders will not influence the result of the quantitative XRD analysis. For the quantitative XRD analysis technique, the purity of leucite powders in the standard is so important that it will affect the validity and accuracy of the measured result. Therefore, the selection of pure leucite for the standards is quite important. Some researchers have employed the natural leucite mineral or leucite-containing frits with known leucite content to prepare the standards. However, the results may be biased due to the impurity of the natural leucite mineral or the changing of leucite content in the frits. More importantly, it is impossible to obtain the same leucite mineral or the frit for the different laboratory. This may lead to the low comparability between the results obtained in the different experiments. Because of the high purity of the materials prepared by the molten method, the leucite synthesized by this method was adopted to fabricate standards for the quantitative XRD analysis in this study. The leucite powders prepared is reproducible and repeatable at different places with the same high purity.

Figure 2 gives the X-ray diffraction patterns for the pure leucite and the standards. The area of all leucite peaks on curve a to d is proportional to leucite content in the standards and the area of copper (111) peak remains constant. The integral area of leucite (211) and (400) peaks was divided by the area of copper (111) peak respectively and these data for the four standards could plot the calibration curves (Fig. 3). The good linear fit (linear regression coefficient, $R = 0.99$, $P < 0.05$) gives the X-ray diffraction patterns for the pure leucite and the standards.

![Fig. 1. XRD patterns of the samples: a. dried precursor b. L_{300} c. L_{650} d. L_{750} e. L_{800} f. L_{900} g. L_{1000} h. L_{1100} i. L_{1200} j. L_{1500}](image-url)
Probability, $P<0.0001$) between peak area ratio (leucite (211)/copper (111) peak area, leucite (400) peak area/copper (111) peak area) and leucite content shows that the leucite content in a powdered specimen (mixed with copper at 9:1) can be obtained by determining the ratio of leucite peak area to copper peak area by using Fig. 3. The slope of the linear fit for leucite (400) peak area/copper (111) peak area vs. leucite content is 1.69, which is very close to 1.73 that has been reported by Rasmussen. The variation may be the result of different balance materials (Rasmussen used silica glass, however, low temperature frit was adopted in the study) in the standards whose absorbance of X-ray is different. Using quantitative XRD, Rasmussen and Markert measured the fraction of leucite by leucite (211) and (400) peak respectively. In this research, the leucite content was measured by the two calibration curves in Fig. 3 respectively and then the average of the two was calculated.

Leucite fraction in the sintered porcelain was determined directly by the method after the porcelain was crushed into powders in an agate mortar and pestle. The determined leucite content in $P_{1100}$ was 25% (Standard Deviation, SD 2%). Figure 4 is the SEM picture of the fracture surface of $P_{1100}$.

![Fig. 2. XRD patterns of S1 (a), S2 (b), S3 (c) and S4 (d) as well as pure leucite (e).](image)

![Fig. 3. Calibration curve for determining leucite content by using internal standard copper. a. Leucite (211) peak area/copper (111) peak area vs. leucite content; b. Leucite (400) peak area/copper (111) peak area vs. leucite content.](image)

Characteristic leucite crystals can be clearly seen with some twinning in the picture. The result of image analysis showed that the content of leucite was 27vol.%. Because the density of leucite is similar to that of dental porcelain, the volume content is approximately equal to the weight content. Therefore, the result of quantitative XRD analysis of leucite content in the dental porcelain is consistent with the image analysis of SEM picture. When measuring leucite content in the synthesized leucite, 40 mass% synthetic leucite powders treated at different temperatures were blended with 60 mass% frit at first. Then, one part of copper was added into the mixture and the obtained mixture was X-rayed. The content of leucite in the synthetic powders could be obtained by multiplying the leucite content in the mixture by 2.5. In this way, the X-ray absorbance of glass phase is incorporated, though at the expense of low accuracy at low leucite content. The determined leucite content in $L_{800}$, $L_{850}$, $L_{900}$, $L_{1000}$ and $L_{1200}$ is illustrated in Fig. 5. According to the quantitative XRD results, leucite content increases with the increasing of treating temperature and it reaches the maximum content at around 1100°C. Since there is no previous work in the literature that has reported the temperature dependence of leucite content, it is impossible to compare the results obtained here with others. However, the content of crystalline phase should increase with the increasing of treating temperature according to the XRD pattern in Fig. 1, which is consistent with the result of quan-

![Fig. 4. SEM pictures of etched fracture surface for $P_{1100}$.](image)
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References


Fig. 5. Leucite content in the synthetic powders at different treatment temperature.