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# THE USE OF SMECTITE CLAYS FOR FORMATION OF A CERAMIC CASE SURROUNDING A TETRAGONAL ZIRCONIUM DIOXIDE CORE

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A novel method for the creation of a case/core ceramic article is described. Coating a smectite-type clay onto an yttria-stabilized zirconia blank, followed by sintering to produce the case/core structure creates this macro-composite. X-ray diffraction results indicate that a properly fabricated article contains a case comprised of monoclinic zirconia (m-ZrO<sub>2</sub>) and zircon (ZrSiO<sub>4</sub>), a core comprised of tetragonal zirconia (t-ZrO<sub>2</sub>), and a gradient between the case and core.

## Introduction

Yttria-stabilized zirconia (YSZ) is a structural ceramic long known for its many technological applications [1, 2]. Its versatility as a structural ceramic is derived from its excellent room-temperature mechanical properties, e.g., high strength, high fracture toughness, superior wear resistance, and chemical inertness. Zirconia-based ceramics can exist in three crystalline polymorphs: monoclinic (m-ZrO<sub>2</sub>), tetragonal (t-ZrO<sub>2</sub>), and cubic (c-ZrO<sub>2</sub>). At room temperature, pure zirconia is monoclinic, and extremely brittle. Alloying with oxides, such as yttria, magnesia, calcia, and ceria, can stabilize the tetragonal and cubic phases of zirconia after heating to a high temperature. Tetragonal ZrO<sub>2</sub> has high toughness, a desirable property for ceramics, whereas c-ZrO<sub>2</sub> has high hardness.

Surface hardness plays a major role in the improvement of wear and abrasion resistance of a material. For tools, and more specifically for cutting tools, it is desirable to have a work surface with sufficient hardness to enhance tool lifetime. Unfortunately, in ceramic materials, an increase in hardness is usually associated with a decrease in toughness. If the hardness is confined to the surface, this dilemma can be overcome. Previously, we have demonstrated that surfaces of YSZ can be modified for improved wear by bringing about a near-surface phase transformation in this material [3]. This improvement was achieved by diffusing magnesia to the surface of YSZ,

transforming the surface into a hard c-ZrO<sub>2</sub> phase without jeopardizing the toughness of the bulk tetragonal phase.

Modifications to YSZ can be adopted for many applications and thus merit consideration for alternative fabrication techniques. As an example, composites of YSZ and alumina are well known for many engineering applications [4]. Magnesia incorporation onto the YSZ-alumina surface results in the formation of c-ZrO<sub>2</sub> along with MgAl<sub>2</sub>O<sub>4</sub> spinel phases, resulting in an increase in wear resistance of this composite [5]. In this paper we describe a novel method for generation of a case/core composite where a smectite clay is coated onto the surface of a YSZ blank followed by sintering [6]. It was desired to make an article that maintained a tough t-ZrO<sub>2</sub> core encased with a hard zircon (ZrSiO<sub>4</sub>) shell. In addition to the case/shell macrostructure, we also investigated the effect of bulk addition of laponite clay to zirconia in an attempt to fabricate a zircon ceramic article.

## Experimental

### *Sample Preparation*

Zirconia green ceramic blanks were fabricated using zirconia powder doped with 3 mole percent Y<sub>2</sub>O<sub>3</sub> (Hanwha Advanced Ceramics, PTY Ltd.). Polyvinyl alcohol, 4 percent by volume, was mixed with the zirconia powder as a binder. The powder was then compacted in a floating mold die press at a pressure of 100 MPa for 30 seconds to make the blank. Some of the blanks were coated with a sol of

Laponite clay,  $\text{Na}_{0.7}(\text{Si}_8\text{Mg}_{5.5}\text{Li}_{0.3}\text{O}_{20}(\text{OH})_4)$ , (Southern Clay Products). Laponite, a hectorite-type smectite clay [7], is a 2:1 layered hydrous magnesium lithium silicate. The Laponite clay sols were prepared by mixing the clay with polyethylene glycol and deionized water. The concentration of clay varied from 4-15 wt. percent. Spin coating of the above sol on the green ceramic blanks was performed at 1,000 rpm. The viscosity of the sol was adjusted using different levels of electrolyte in order to control the depth of penetration of the sol into the zirconia blank. The spin-coated green ceramic blanks were then dried in an oven at 100EC before placing on a zirconia plate and sintering at 1,500EC for 2 hours.

Samples were also generated by mixing the above mentioned zirconia powder with Laponite clay powder in weight ratios of 100:0, 98:2, 90:10, and 50:50 zirconia/clay. After addition of the polyvinyl alcohol binder, green ceramic blanks were fabricated then sintered as previously mentioned.

#### X-ray Diffraction

Phase identification of all samples was carried out using X-ray diffraction (XRD). Data were collected using a Rigaku RU-300 diffractometer equipped with a copper rotating anode, diffracted beam graphite monochromator tuned to  $\text{CuK}\alpha$  radiation, and scintillation detector. Coupled  $2\theta/2\theta$  scans were used to detect the phases present in the bulk sample. Glancing angle scans were collected to detect phases present in the case. Data were analyzed using Jade 3.1 software [8] and phases were identified by comparison to the Powder Diffraction File [9].

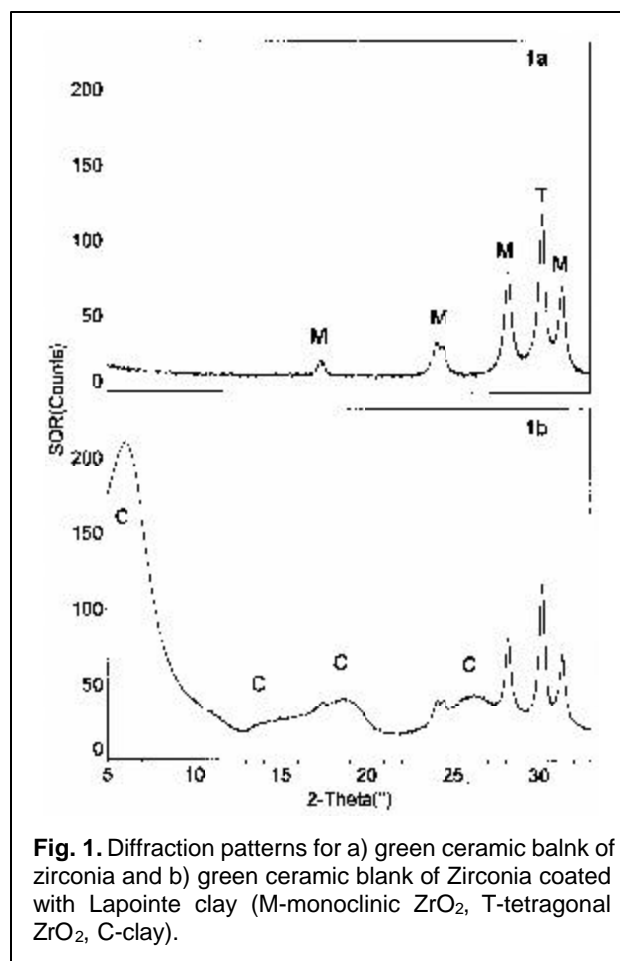
#### Scanning Electron Microscopy

Surface morphology was evaluated using a JEOL 6100 scanning electron microscope equipped with a secondary electron detector.

### Results and Discussion

In Fig. 1, the diffraction patterns for unsintered ceramic blanks of zirconia (Fig. 1a) and zirconia with a spin coating of Laponite (Fig. 1b) are shown. The diffraction patterns indicate that the unsintered zirconia contains both monoclinic ( $\text{m-ZrO}_2$ ) and tetragonal ( $\text{t-ZrO}_2$ ) Polymorphs. Based on the method of Garvie et al. [10], the percent  $\text{m-ZrO}_2$  can be determined by:

$$X = \frac{\{I_m(111) + I_m(1\bar{1}\bar{1})\}}{\{I_t(111) + I_m(111) + I_m(1\bar{1}\bar{1})\}} \quad (1)$$

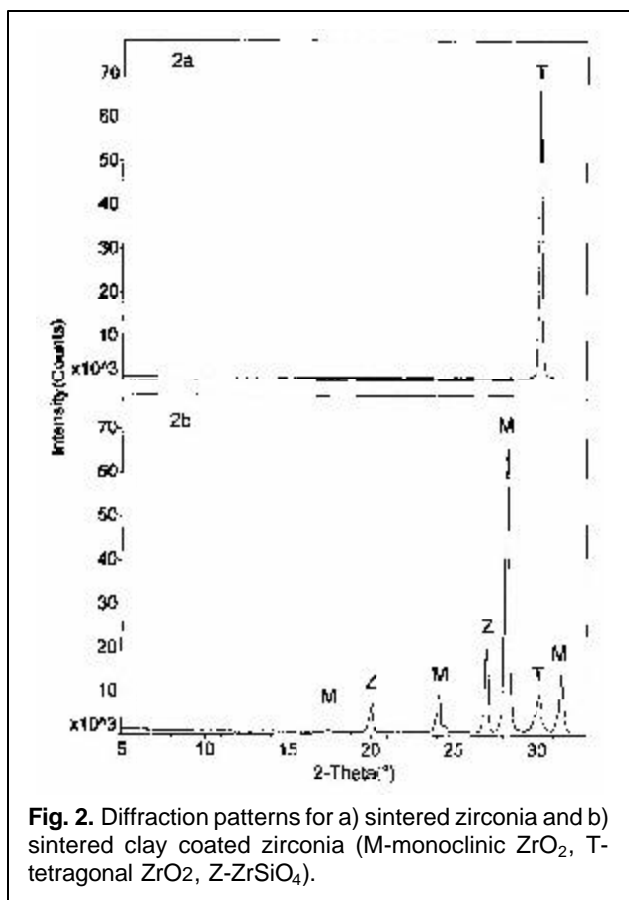


**Fig. 1.** Diffraction patterns for a) green ceramic blank of zirconia and b) green ceramic blank of Zirconia coated with Laponite clay (M-monoclinic  $\text{ZrO}_2$ , T-tetragonal  $\text{ZrO}_2$ , C-clay).

where  $I_m(\text{hkl})$  and  $I_t(\text{hkl})$  are the integrated intensities of the  $\text{hkl}$  peaks of the monoclinic and tetragonal  $\text{ZrO}_2$  phases respectively. For the samples shown in Fig. 1, the percent  $\text{m-ZrO}_2$  was found to be 50%. When laponite is spin coated onto the blank ceramic surface, there is no change in the zirconia phase composition prior to sintering. The clay surface layer shows (001) preferred orientation in the XRD pattern (Fig. 1b), as evidenced by the existence of a strong clay (001) basal plane diffraction peak at  $6.5^\circ 2\theta$  ( $13.6 \text{ D}$ ).

Upon sintering, the neat zirconia sample is observed to contain only  $\text{t-ZrO}_2$  indicating that all of the  $\text{m-ZrO}_2$  has transformed to the  $\text{t-ZrO}_2$  phase (Fig. 2a). The clay surface coated sample provides a different result. The major component in the case of this sample is  $\text{m-ZrO}_2$ , along with a moderate amount of  $\text{ZrSiO}_4$  and a minor amount of  $\text{t-ZrO}_2$ . The original intent of the clay surface coating was to generate a  $\text{ZrSiO}_4$  case.

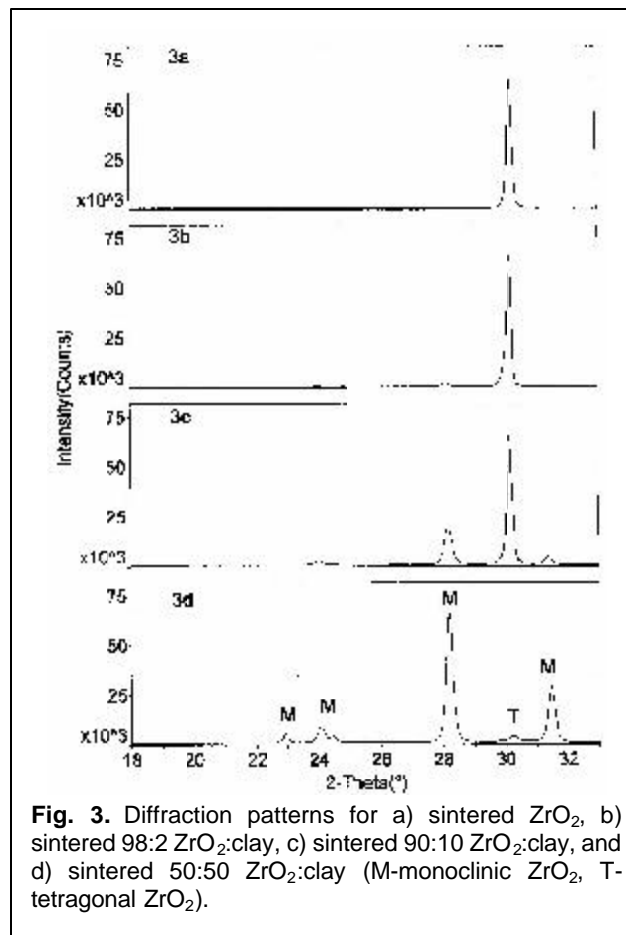
The results in Fig. 2b indicate that this methodology is successful in generating zircon on the



**Fig. 2.** Diffraction patterns for a) sintered zirconia and b) sintered clay coated zirconia (M-monoclinic  $ZrO_2$ , T-tetragonal  $ZrO_2$ , Z- $ZrSiO_4$ ).

ceramic surface as a case component, as desired, but the presence of the m- $ZrO_2$  was unexpected. The backside of both samples, 2a and 2b, were analyzed by XRD and found to be phase pure t- $ZrO_2$ . Since the sintered neat zirconia sample has only t- $ZrO_2$  present, it appears that a t- $ZrO_2$  to m- $ZrO_2$  phase transition occurred in the case of the clay coated  $ZrO_2$  sample as a result of the presence of the clay. The phase transition of t- $ZrO_2$  to m- $ZrO_2$  is often associated with an applied stress on the t- $ZrO_2$  component of such a ceramic article [11]. However, since there was no stress applied, a chemical induced stress (or phase transition) must have been created during the sintering process.

In an effort to further investigate the formation of m- $ZrO_2$  and  $ZrSiO_4$  in clay containing zirconia ceramic articles, bulk mixtures of  $ZrO_2$ /clay were generated. X-ray diffraction patterns for these samples after sintering are shown in Figs. 3a-d. In the case of 100%  $ZrO_2$ , t- $ZrO_2$  was the only phase observed to be present (Fig. 3a) as expected. When the  $ZrO_2$ :clay ratio was 98:2, the presence of a low-intensity diffraction peak at  $\sim 28.2^\circ$  (Fig. 3b) is an indication that a small amount of m- $ZrO_2$  has been



**Fig. 3.** Diffraction patterns for a) sintered  $ZrO_2$ , b) sintered 98:2  $ZrO_2$ :clay, c) sintered 90:10  $ZrO_2$ :clay, and d) sintered 50:50  $ZrO_2$ :clay (M-monoclinic  $ZrO_2$ , T-tetragonal  $ZrO_2$ ).

generated along with the remaining major phase t- $ZrO_2$ . As the weight fraction of clay increased, 90:10  $ZrO_2$ :clay (Fig. 3c) and 50:50  $ZrO_2$ :clay (Fig. 3d), the fraction of m- $ZrO_2$  also increased. However, there is no evidence of  $ZrSiO_4$  or other crystalline phases in any of these  $ZrO_2$ :clay bulk samples. In a sample of 10:90  $ZrO_2$ :clay, the  $ZrO_2$  was all m- $ZrO_2$  and  $ZrSiO_4$  was not detected. Table 1 lists the percent m- $ZrO_2$  and t- $ZrO_2$  phases corresponding to  $ZrO_2$ :clay ratios for the above bulk samples. It is worth noting that high levels of clay (>70wt%) in  $ZrO_2$  weakens the physical integrity of the sample as the ceramic blank flows during sintering.

The absence of a  $SiO_x$  crystalline phase in samples 3b-d was puzzling, particularly at levels of 50wt% clay. Analysis of samples 3b-d by X-ray fluorescence (XRF) showed a strong  $SiK\alpha$  peak indicating percent levels of Si being present in the samples. One consideration was the possibility of Si incorporation in the m- $ZrO_2$  lattice. To see if unit cell changes occurred, lattice constant cell refinement [12] of the m- $ZrO_2$  phase in samples 3b-d was performed. The refinement results shown in Table 2

indicate that there is no statistically significant change in the m-ZrO<sub>2</sub> unit cell as a function of the bulk ZrO<sub>2</sub>:clay ratio for the sintered samples. Apparently, little or no Si incorporated into the zirconia lattice. Samples 3a and 3d were analyzed using infrared analysis. Sample 3a (100% ZrO<sub>2</sub>) was found to be absent of any SiO<sub>x</sub> containing phase, whereas sample 3d (50: 50 ZrO<sub>2</sub>:clay) had a Si-O stretch at 1,150 cm<sup>-1</sup> consistent with the presence of a silicate phase. Putting these results together, it is believed that the sintering of bulk ZrO<sub>2</sub>:clay ceramics results in the formation of an amorphous silicate phase, along with the crystalline zirconia phases.

An analogous result was reported by Latella et al. [13] for liquid-phase sintered (LPS) aluminas where β-spodumene (Li<sub>2</sub>Al<sub>2</sub>Si<sub>4</sub>O<sub>12</sub>) was utilized as a lithium-bearing flux [14]. In Latelia's study, it was observed that a 95:5 alumina: β-spodumene bulk mixture sintered at 1,450EC contained 6.8% glass after LPS processing. The results described here in the present study suggest that Laponite clay may be demonstrating flux-like properties in the zirconia:clay matrix when sintered. Upon cooling, the silicate resulting from the clay remains amorphous but due to

differences in thermal expansion, stresses could be developed at the zirconia/silicate interface resulting in the phase transformation of t-ZrO<sub>2</sub> to m-ZrO<sub>2</sub>.

The results of the bulk ZrO<sub>2</sub>:clay samples (refer to Figs. 3b-d) provide insight into the generation of m-ZrO<sub>2</sub> in the bulk and surface coated ZrO<sub>2</sub> samples after the sintering process, but fail to explain why generation of ZrSiO<sub>4</sub> is observed only when clay is deposited onto the surface of the zirconia ceramic blank before sintering (refer to Fig. 2b). Scanning electron micrographs of sintered samples show significant difference in surface morphology depending upon clay incorporation on the surface (Fig. 4a) or in the bulk (Fig. 4b) of the ZrO<sub>2</sub>. In the case of sintered clay deposited on the ZrO<sub>2</sub> surface, small spherical grains (nominal size 0.5 microns) cover the entire surface. For the bulk ZrO<sub>2</sub>:clay sample, large grains (>10 microns) are predominant along with small patches of 2 micron spherical grains. Based on the above results, it appears that the generation of ZrSiO<sub>4</sub> in a ZrO<sub>2</sub>:clay matrix only occurs when clay is coated onto the ZrO<sub>2</sub> blank. At the interface of this coating, one has 100% clay next to 100% ZrO<sub>2</sub>. Although it is not clear at this time why this specific sample preparation matrix must be utilized for formation of zircon, the excess SiO<sub>2</sub> at the ZrO<sub>2</sub> surface may be driving the reaction to generate zircon along with converting t-ZrO<sub>2</sub> to m-ZrO<sub>2</sub>.

## Summary

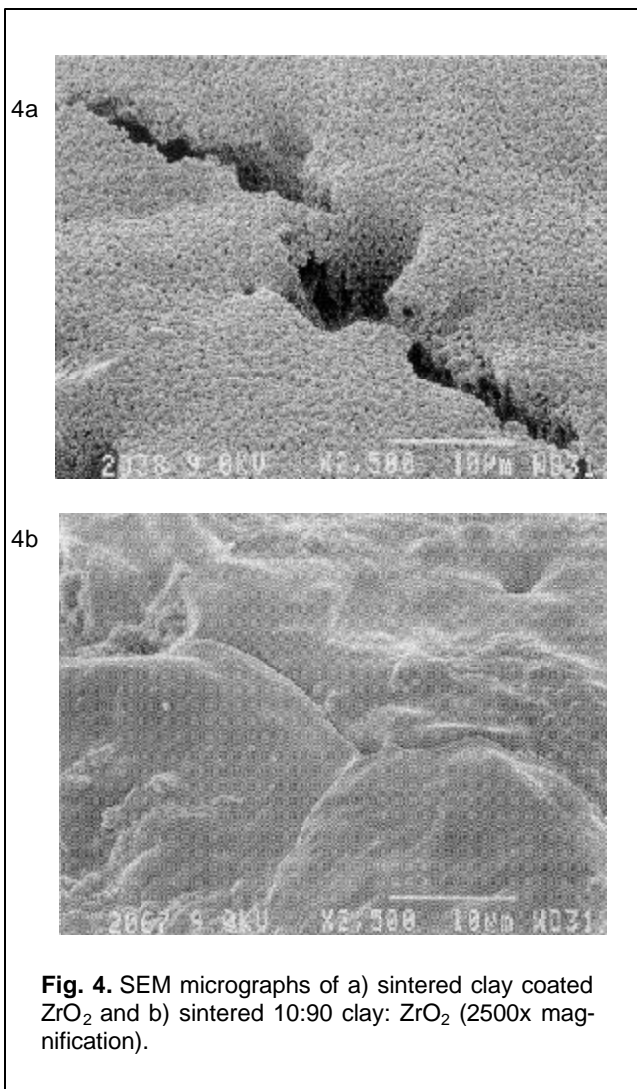
The ability to fabricate a ceramic article with an outer case containing predominately m-ZrO<sub>2</sub> and ZrSiO<sub>4</sub> and a t-ZrO<sub>2</sub> core has been demonstrated. Zircon is a result of a chemical reaction between ZrO<sub>2</sub> and SiO<sub>2</sub> whereas the conversion of t-ZrO<sub>2</sub> is due to thermal expansion coefficient differences between ZrO<sub>2</sub> and a glassy silicate that forms when the clay is melted. The method utilizes a deposition of Laponite clay on a ZrO<sub>2</sub> blank prior to sintering. The ZrO<sub>2</sub>:clay

**Table 1.** Percent m-ZrO<sub>2</sub>, t-ZrO<sub>2</sub> for sintered bulk ZrO<sub>2</sub>:clay samples

ZrO <sub>2</sub> :clay bulk ratio (wt:wt)	m-ZrO <sub>2</sub> (%)	t-ZrO <sub>2</sub> (%)
100:0	0	100
98:2	4	96
90:10	34	66
50:50	96	4
10:90	100	0

**Table 2.** Refined unit cell parameters for m-ZrO<sub>2</sub> phase in ZrO<sub>2</sub>:clay bulk samples after sintering

ZrO <sub>2</sub> :clay bulk ratio (wt:wt)	a (D)	b (D)	c (D)	β (E)	Volume (D <sub>3</sub> )
98:2	5.137(4)	5.190(5)	5.308(7)	99.08(8)	139.8
90:10	5.140(3)	5.195(3)	5.314(3)	99.06(5)	140.1
50:50	5.152(2)	5.202(2)	5.316(2)	99.20(3)	140.6
m-ZrO <sub>2</sub> PDF card 78-0047	5.151	5.203	5.316	99.19	140.6



**Fig. 4.** SEM micrographs of a) sintered clay coated  $ZrO_2$  and b) sintered 10:90 clay:  $ZrO_2$  (2500x magnification).

interface, which results from this deposition, is critical for  $ZrSiO_4$  to form. If the  $ZrO_2$ : clay article is randomly mixed before sintering,  $ZrSiO_4$  is not observed to be present. In these bulk samples  $mZrO_2$  increases in weight fraction as the weight fraction of clay is increased. Too much clay will cause the ceramic article to lose shape and flow.

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## References

- [1] Nettleship and R. Stevens, *Int. J. High Technol. Ceram.*, **3** (1987) 1.
- [2] R. Stevens, *Zirconia and Zirconia Ceramics*, Pub. No. 113 (Magnesium Elektron Inc., Flemington, NJ, 1986).
- [3] D. Chatterjee, D. Majumdar, and S. Ghosh, *Surf. Coat. Technol.*, **54/55** (1992) 516.
- [4] R. Stevens, in: *Ceramics and Glasses*, Vol. 4 of *Engineered Materials Handbook* (ASM, Cleveland, OH, 1991)p.775.
- [5] D. Majumdar, D. Chatterjee, S. Ghosh, and T Blanton, *Appl. Surf. Sci.*, **68** (1993) 189.
- [6] D. Chatterjee, D. Majumdar, and T. Blanton, U.S. Patent 5,798,308, (August 25, 1998).
- [7] G. W. Brindley, *Crystal Structures of Clay Minerals and their X-ray Identification*, G. W. Brindley and G. Brown eds., Spottiswoode Ballantyne Ltd., London (1984) 178.
- [8] Jade 3.1, Materials Data Inc., Livermore CA. (1998).
- [9] Powder Diffraction File, International Centre for Diffraction Data, Newtown Square, PA (1999).
- [10] R. C. Garvie and P. S. Nicholson, *J. Amer. Cer. Soc.*, **55**(6) (1972) 303.
- [11] R. C. Garvie, R. H. J. Hannik, and M. V. Swain, *J. Mat. Sci. Lett.*, **1** (1982) 437.
- [12] D. E. Appleman and H. T Evans, Report PB216188, U. S. Department of Commerce, National Technical Information Service, 5825 Port Royal Road, Springfield, VA 22151, USA (1973).
- [13] B. A. Latella, G. R. Burton, and B. H. O'Connor, *J. Am. Ceram. Soc.*, **78**(7) (1995) 1895.
- [14] S. Knickerbocker, M. Tuzzolo, and S. Lawhorne, *J. Am. Ceram. Soc.*, **72**(10) (1989) 1873.