

## A preparation of hexacelsian powder by solution-polymerization route and its phase transformation behavior

Sang-Jin Lee and Young-Soo Yoon\*

*Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA*

*\*Ceramics Division, Korea Institute of Science and Technology, Seoul 130-650, Korea*

## Solution-polymerization 방법에 의한 hexacelsian 분말의 합성 및 상전이 공정에 의한 celsian 소결체의 제조

이상진, 윤영수\*

일리노이 주립대학 재료공학과, 어바나샴페인, U.S.A.

\*한국과학기술원 세라믹스 연구부, 서울, 130-650

**Abstract** Hexacelsian ( $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) powder was prepared by a solution-polymerization route employing PVA solution as a polymeric carrier. A fine amorphous-type hexacelsian powder with an average particle size of  $0.8 \mu\text{m}$  and a BET specific surface area of  $63 \text{ m}^2/\text{g}$  was made by a ball-milling the powder precursor for 12 h after calcination at  $800^\circ\text{C}$  for 1 h. A densified hexacelsian was obtained through sintering at  $1550^\circ\text{C}$  for 2 h under an air atmosphere. The  $\alpha \leftrightarrow \beta$  and  $\beta \leftrightarrow \gamma$  displacive phase transformation in polycrystalline hexacelsian was examined by using dilatometry and differential scanning calorimetry. The reconstructive transformation between hexacelsian and celsian was obtained by annealing at  $1600^\circ\text{C}$  for 72 h. Volume contraction of 5.6 % was accompanied by the reconstructive transformation.

**요약** 약  $0.8 \mu\text{m}$ 의 평균입자크기와  $63 \text{ m}^2/\text{g}$ 의 비표면적을 갖는 소결성이 뛰어난 hexacelsian 분말이 solution-polymerization 방법에 의해 제조되어졌다. Polymerization 공정을 통한 분말합성을 위하여 PVA 용액이 사용되어졌다. 소결후 치밀화된 hexacelsian은  $\alpha$ ,  $\beta$ ,  $\gamma$  간의 상전이

거동을 보였고, 상대밀도 98.5 %의 치밀화된 celsian 소결체가 1600 °C에서 72시간의 서냉공정을 거쳐 hexacelsian의 상전이에 의하여 얻어졌다.

## 1. Introduction

Hexacelsian,  $\text{BaAl}_2\text{Si}_2\text{O}_8$ , the high temperature polymorph of barium feldspar, possesses a interesting layered crystal structure and at least one significant displacive phase transformation [1]. There are four known polymorphs of  $\text{BaAl}_2\text{Si}_2\text{O}_8$ . Celsian and paracelsian occur naturally as minerals [2]. Celsian is the thermodynamically stable phase under ambient conditions. It is a framework aluminosilicate and a member of the feldspar group. In natural samples, K and Si frequently substitute for Ba and Al. Feldspars in the  $\text{KAlSi}_3\text{O}_8$ - $\text{BaAl}_2\text{O}_8$  solid solution series with <30 %  $\text{BaAl}_2\text{Si}_2\text{O}_8$  are given the mineral name hyalophane, while celsian refers to compositions with > 90 %  $\text{BaAl}_2\text{Si}_2\text{O}_8$ . Feldspars with intermediate compositions are very rare in nature [3]. Paracelsian is a less common mineral and is believed to be metastable at all temperatures under ambient pressure [4]. The structure consists of chains of tetrahedra similar to those found in the stable phase. Hexacelsian is the stable high temperature phase of  $\text{BaAl}_2\text{Si}_2\text{O}_8$  existing under equilibrium conditions between 1590°C and the melting point, 1760°C [4-6]. Hexacelsian is structurally quite different from celsian and paracelsian. In fact it is not a true framework silicate despite the fact that there are no non-bridging oxygens in the structure. It is composed of

double layer sheets of  $(\text{Al}, \text{Si})\text{O}_4$  tetrahedra with the barium cations located between the layers. Due to the reconstructive nature of the hexacelsian→celsian transformation, hexacelsian is easily retained as a metastable phase to room temperature [7].

Transformation of hexacelsian is illustrated in Fig. 1. The sluggishness of the hexacelsian to celsian reconstructive transformation requires the prolonged heat treatment of samples in order to obtain the celsian phase. This sluggishness of the phase transformation should be advantageous in the retention of the hexacelsian phase allowing the displacive transformation to be utilized. Currently there is great interest in using the feldspar phase, celsian, as a matrix material for ceramic matrix composites

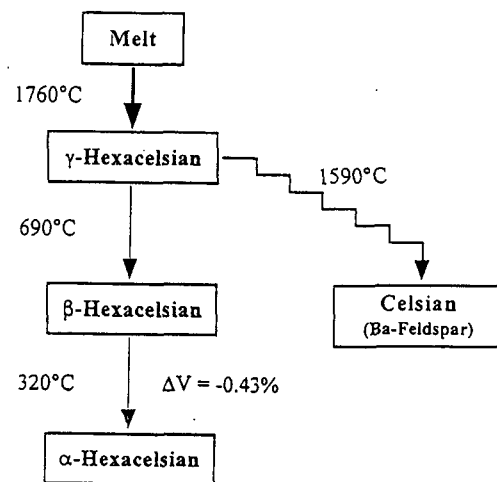


Fig. 1. Transformation sequence for hexacelsian.

due to its refractoriness and low thermal expansion coefficient [8-10]. The ability of celsian to be processed as a glass-ceramic [11,12] is also very attractive. However, the use of celsian as a matrix is made difficult because the hexacelsian phase always crystallizes first during synthesis.

Recently, the hexacelsian to celsian reconstructive transformation is used for shear-induced transformation weakening [13]. This behavior makes it a promising candidate for use as an interfacial material for oxide/oxide fiber reinforced composites, since hexacelsian can function as both a transformable interphase and as a cleavable interphase. This mechanism, called "reconstructive transformation toughening," uses a volume reducing reconstructive phase transformation to generate tensile stresses at the interfaces in composites. The most significant advantage of this new mechanism is that it is relatively insensitive to changes in temperature.

In this work, the preparation of a fine and homogeneous hexacelsian powder by a solution-polymerization route [14-17] is discussed. The solution-polymerization route, better known as "Pechini type" process, [18, 19] was suggested to produce a stable and atomistically homogeneous powder without the use of expensive and unstable alkoxides. Furthermore, the process is very simple and low cost. In this work, a better simple-structured and inexpensive polymer, polyvinyl alcohol (PVA), is also used as the organic carrier of the pre-ceramic powder instead of Pechini resin. The PVA polymer, which is a

non-chelating polymer having large chain molecules as the polymeric carrier, has hydroxyl functional groups [14,20]. A steric entrapment of the metal ions is achieved by using these large chain molecules [14, 16]. This is suggested to form a soft and bulky precursor.

The aim of this study is to prepare a fine and pure hexacelsian powder by the solution-polymerization route and synthesize a celsian through reconstructive transformation. The transformation behavior are evaluated by X-ray diffractometry (XRD), differential scanning calorimetry (DSC) and dilatometry.

## 2. Experimental procedure

### 2.1. Powder preparation and sintering

The hexacelsian powder was synthesized by the solution-polymerization method. A clear sol was prepared from Ludox SK Colloidal silica (25 wt% suspension in water, Du Pont Chemicals, Wilmington, DE) as a source of silica, barium nitrate ( $\text{Ba}(\text{NO}_3)_2$ , reagent grade, Aldrich Chemical Co., Milwaukee, WI), and lactic acid, aluminum salt ( $[\text{CH}_3\text{CH}(\text{OH})\text{CO}_2]\text{Al}$ , reagent grade, Aldrich Chemical Co., Milwaukee, WI) in stoichiometric proportion. After mixture of these reagents with DI water, a polymeric carrier was added, and then the mixture was heated up to 120°C.

As a polymeric carrier, PVA solution was added to the mixture. The PVA solution was

made from 5 wt% PVA (degree of polymerization-1700) dissolved in water. The amount of the PVA to cation sources in the solution were adjusted in such a way that there were 4 times more positively charged valences of the cations than the negatively charged functional ends of the organics [14]. As the viscosity of the mixture solution increased by evaporation of water, the mixture was vigorously stirred. The remaining water was then dried, transforming the gel into a porous solid.

Finally, the precursor was crushed and heated up to 800 °C for calcination. To produce finer particle, the calcined powder was subjected to ball-milling for 12 h. The polyethylene jar, which has a volume of 1500 ml, included 50 g calcined powder with 1.5 kg zirconia ball media (ball diameter : 5 mm). Isopropyl alcohol was used as a solvent for milling. The ball milled and dried powder was uniaxially pressed at 20 MPa followed by iso-static pressing at 170 MPa for 10 min. The pellet-shaped green compact was sintered at 1550°C for 2 h under an air atmosphere, and finally the furnace was cooled down to room temperature. After sintering, the sample was subjected to annealing at 1600°C for various times.

## 2.2. Characterization

(A) Thermal Analysis : The pyrolysis and decomposition behavior of crushed precursor were monitored by simultaneous differential thermal analysis and thermogravimetric analysis (DTA/TGA) (Model STA 409, Net-

zsch GmbH, Selb, Germany) up to 1400°C at a heating rate of 5°C/min, in an air atmosphere. The thermal analysis of polycrystalline hexacelsian was examined by differential scanning calorimetry (DSC) (Model STA 409, Netzsch GmbH, Selb, Germany).

(B) Specific Surface Area Measurement : The specific surface areas of the calcined powders of pre or post ball-milling were measured by nitrogen gas absorption (Model ASAP 2400, Micromeritics, Norcross, GA). The surface area data were obtained by five-point BET analysis.

(C) Particle Size Distribution Analysis : The particle size distributions of the calcined powders of pre or post ball-milling were examined by X-ray absorption spectrometry (Sedigraph Model 5000E, Micromeritics). The powders were suspended in a calibrated dispersion liquid. The suspensions were ultrasonicated for 3 min before analysis.

(D) X-ray Diffraction Analysis : The development of crystalline phase and phase transformation were studied by using a Rigaku spectrometer (DMax automated powder diffractometer, Rigaku/USA, Danvers, MA) with CuK $\alpha$  radiation (40 kV, 40 mA).

(E) Thermal Expansion Behavior : The thermal expansion behavior of sintered polycrystalline hexacelsian sample was determined with a recording dilatometry (Netzsch Dilatometry, 402E, Germany) up to 1200°C at a heating rate of 5°C/min.

(F) Linear Shrinkage Behavior : The linear shrinkage of each specimen was measured by determining the dimensions with

vernier callipers.

(G) Relative Density Measurement: The density for the sintered specimen was estimated by the Archimedes' method using distilled water as a displacement liquid. The relative density of sintered hexacelsian and celsian was calculated from the density of the hexacelsian and celsian ( $3.30 \text{ g/cm}^3$  and  $3.39 \text{ g/cm}^3$ , respectively) as a theoretical density [21,22]

(H) Electron Microscopy: The powder morphology and microstructure of sintered hexacelsian were examined by scanning electron microscopy, (SEM, ISI DS-130, International Scientific Instruments, Santa Clara, CA).

### 3. Results and discussion

In the synthesis of hexacelsian, barium nitrate and lactic acid, aluminum salt were used as the  $\text{Ba}^{2+}$  and  $\text{Al}^{3+}$  source because of their excellent solubility in cold water [23]. Ludox SK was also chosen as the silica source because of solubility consideration. In general, colloidal silica showed good solubility in cold water at low pH condition. Ludox SK has lower pH, 4-5, than other Ludox colloidal silica source.

Figure 2 shows the DTA and TGA results for a hexacelsian precursor derived from PVA solution process. The thermal analysis revealed a two step weight loss with corresponding exothermic curves. The first weight loss was observed until  $150^\circ\text{C}$  temperature. This was associated with

decomposition of residual  $\text{NO}_x$  compounds, from nitrate salt. Most of decomposed  $\text{NO}_x$  compounds were removed during stirring process on the high-viscosity sol condition. The measuring temperature of this condition was about  $110\text{-}120^\circ\text{C}$ . The second major weight loss in TGA occurred between  $250^\circ\text{C}$  and  $500^\circ\text{C}$  with a corresponding exotherm in the DTA curve. The weight loss was caused by the burnout of the pyrolyzed organic carrier, PVA. The weight loss was continued until  $800^\circ\text{C}$  due to some residual carbon. A small exothermic peak, which is associated with crystallization, was detected at around  $900^\circ\text{C}$ .

Figure 3 shows SEM photographs and particle size distribution of both calcined powders of pre and post ball-milling. In case of the pre ball-milled, calcined powder showed a broad particle size distribution and irregular shape with agglomeration. The ball-milled powder showed comparatively narrower particle size distribution, and had an average particle size of about  $0.8 \mu\text{m}$ . The

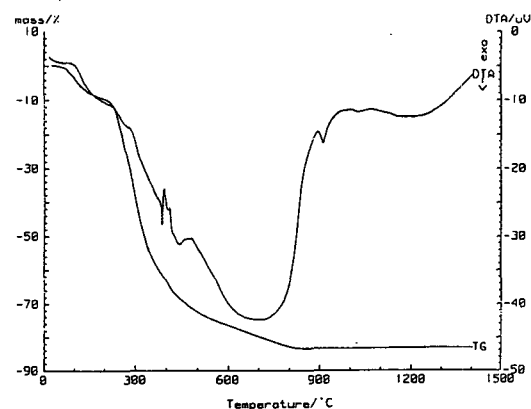


Fig. 2. Simultaneous DTA/TGA analysis of hexacelsian precursor.

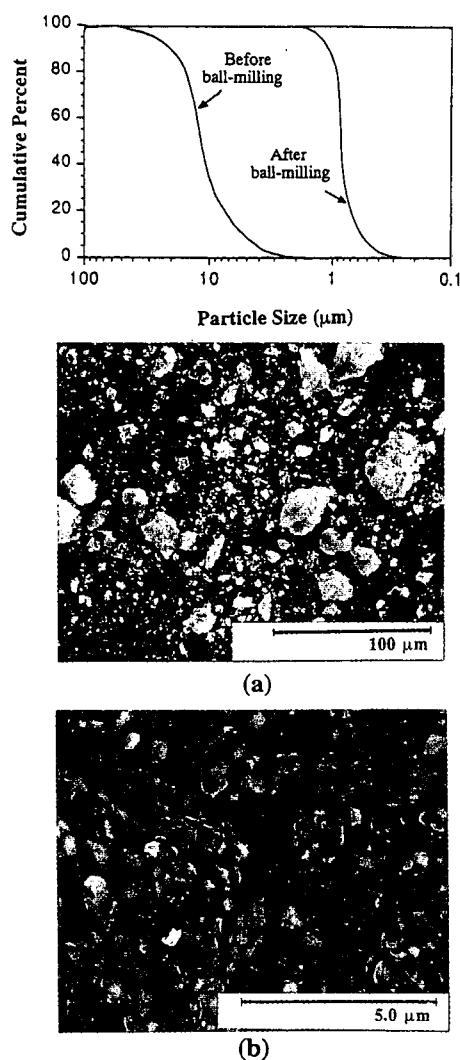


Fig. 3. Particle size distribution and SEM micrographs of calcined hexacelsian powder (a) before ball-milling and (b) after ball-milling.

BET specific surface area of the calcined and ball-milled powder were  $32 \text{ m}^2/\text{g}$  and  $63 \text{ m}^2/\text{g}$ , respectively. The high specific surface area of the pre ball-milled, calcined powder, in spite of its larger average particle size than the ball-milled powder, implies that the

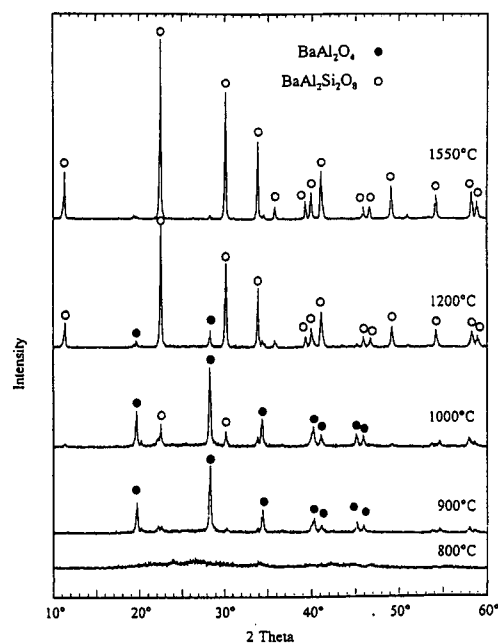


Fig. 4. X-ray diffraction patterns showing the development of crystalline hexacelsian as a function of heating temperature. Hold-time at each temperature was 2 h.

calcined powder was quite porous. The submicron particles after ball-milling were attributed to the soft and porous nature of the calcined powder.

Figure 4 shows development of crystalline phases from the precursor at various heating temperatures. An amorphous phase was observed at  $800^\circ\text{C}$ . Between  $900^\circ\text{C}$  and  $1100^\circ\text{C}$ , the intermediate phase,  $\text{BaAl}_2\text{O}_4$ , was observed to crystallize along with hexacelsian. Above  $1200^\circ\text{C}$  hexacelsian peaks were detected as major phase. With increasing temperature the amount of hexacelsian phase increased gradually and the hexacelsian peaks were developed almost completely at  $1550^\circ\text{C}$ .

DSC and dilatometry analyses of polycrystalline hexacelsian sintered at 1550°C for 2 h indicated not one but two first order transformation. Dilatometry plots for hexacelsian are shown in fig. 5. The transformation at  $\sim 320^\circ\text{C}$  was accompanied by a volume change of 0.42 % with a decrease in volume on cooling. Thermal expansion coefficient was also changed largely at this phase transformation point. The second transformation had a negligible volume change. The DSC curves for an identically prepared sample are shown in Fig. 6. Both transformations were clearly seen here. The very small enthalpy of transformation was likely the reason that the transformation at  $\sim 690^\circ\text{C}$  has

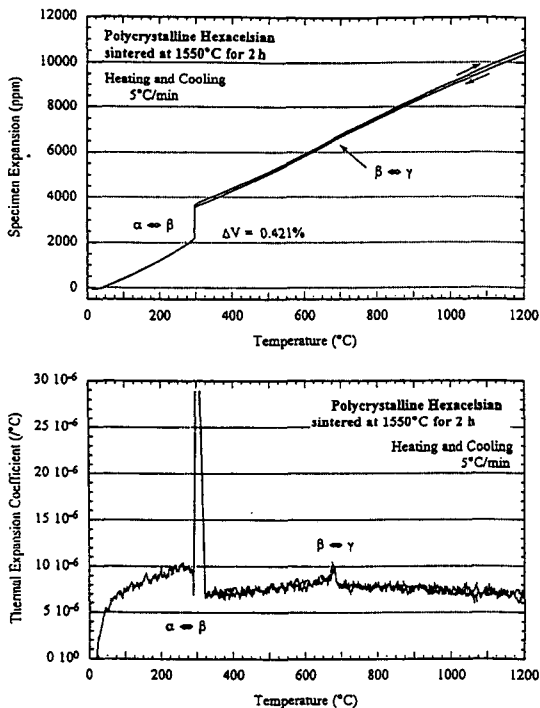


Fig. 5. Dilatometry curves for polycrystalline hexacelsian sample sintered at 1550°C for 2 h.

not been previously detected. As the graphs (Fig. 5) show, the thermal expansion coefficient of hexacelsian was approximately  $8.0 \times 10^{-6}/^\circ\text{C}$ .

The trend in variation of shrinkage of the amorphous-type hexacelsian powder compact at various sintering temperatures is shown in Fig. 7. The minimum sintering con-

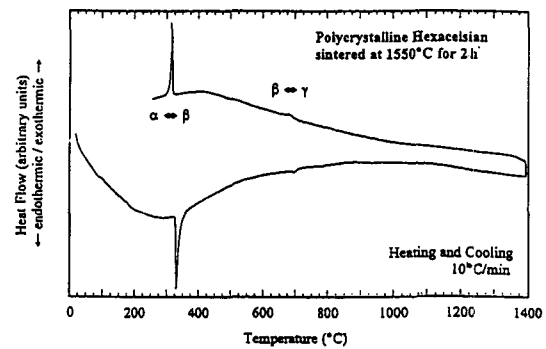


Fig. 6. DSC curves for polycrystalline hexacelsian sintered at 1550°C for 2 h.

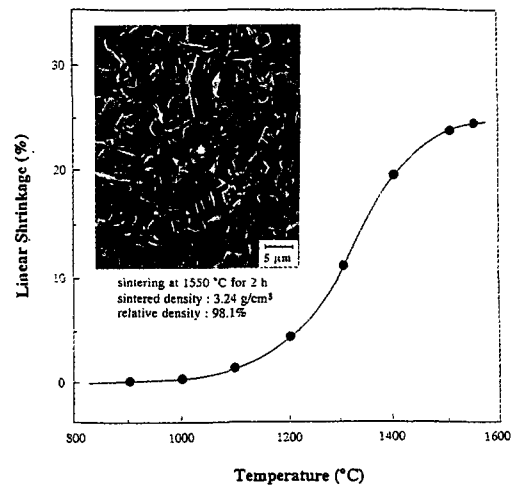


Fig. 7. Shrinkage behavior and micrograph of fracture surface for densified hexacelsian. The densified hexacelsian (sintered density :  $3.24 \text{ g/cm}^3$ , relative density : 98.1 %) was sintered at 1550°C for 2 h.

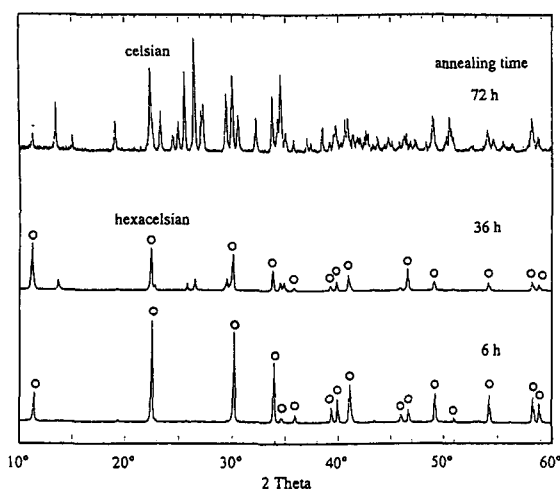


Fig. 8. X-ray diffraction profiles for polycrystalline hexacelsian annealed at 1600°C as a function of annealing time. The density of celsian synthesized after annealing for 72 h was 3.34 g/cm<sup>3</sup>(relative density : 98.5 %).

dition required to produce dense polycrystalline hexacelsian was 1550°C for 2 h for the laboratory synthesized powder. The microstructure of dense pellet after sintering is also displayed in Fig. 7. The relative density of the densified hexacelsian was 98.1 %.

Finally, hexacelsian → celsian reconstructive transformation was examined by X-ray diffraction. Figure 8 shows the transformation behavior of sintered hexacelsian sample after annealing at 1600°C. It is known that the equilibrium ( $\gamma$ ) structure exists above 1590°C when it converts to the celsian structure by a slow, sluggish, reconstructive transformation mechanism. If the kinetics are such that insufficient time is allowed for the reconstructive transformation, the  $\gamma$  phase can be retained metastably down to room temperature. An estimated -5.6 % vol-

ume contraction on transformation during cooling was calculated by the change of lattice parameter on the base of JCPDS data [21,22]. With increasing annealing time, celsian phase increased gradually while hexacelsian phase decreased (Fig. 8). After 72 h the polycrystalline hexacelsian was mostly converted to celsian. The measured thermal expansion coefficient by using dilatometry was about  $4.0 \times 10^{-6}/^{\circ}\text{C}$

#### 4. Conclusions

Solution-polymerization technique has been employed for the preparation of hexacelsian powder. The powder, calcined at 800 °C for 1 h, could be easily milled to submicron particle sizes. This indicated that a fine and homogeneous hexacelsian powder can be produced by polymerization route using the mechanism of stearic entrapment of the metal ions by hydroxyl functional groups. The large chain molecules of PVA acted as a effective polymeric carrier in the solution-polymerization technique in spite of the small content in the sol solution.

Densified celsian pellet with a relative density of 98.5 % was obtained by 72 h annealing times at 1600°C from the synthesized hexacelsian.

#### References

- [ 1 ] R.E. Newnham and H.D. Megaw, Acta Crystal 13 (1960) 303.



- [ 2 ] G. Chiari, G. Gazzoni, J.R. Craig, G.V. Gibbs and S.J. Louisnathan, *Am. Mineral.* 70 (1985) 969.
- [ 3 ] W.A. Deer, R.A. Howie and J. Zussman, *Rock Form. Minerals.* 4 (1963) 166.
- [ 4 ] H.C. Lin and W.R. Foster, *Am. Mineral. Soc.* 53 (1968) 134.
- [ 5 ] C.E. Semler and W.R. Foster, *J. Am Ceram. Soc.* 52 (1969) 679.
- [ 6 ] C.E. Semler and W.R. Foster, *J. Am Ceram. Soc.* 53 (1970) 549.
- [ 7 ] G. Oehlschlege and K. Abraham, *Kristall und Technik.* 11 (1976) 59.
- [ 8 ] L. Zhien, H. Ying and Y. Jianjun, *J. Mater. Sci.* 30 (1995) 405.
- [ 9 ] A. Bandyopadhyay, S.W. Quander, P. B. Aswath and D.L. Hunn, *Scripta Metall. et Mater.* 32 (1995) 1256.
- [10] A. Bandyopadhyay, P.B. Aswath, W. D. Porter and O.B. Cavin, *J. Mater. Res.* 10 (1995) 1256.
- [11] J.J. Buzniak, R.M. Dickerson, K.P.D. Lagerlof and N.P. Bansal, *Advances in Ceramic-Matrix Composites II.* (American Ceramic Society, Westerville, OH 1994) p.411.
- [12] L. Barbieri, A.B. Corradi, C. Leonelli, T. Manfredini and C. Siligardi, *Mater. Res. Bull.* 30 (1995) 27.
- [13] J.L. Shull, Ph.D Thesis, Univ. of Illinois at Urbana-Champaign. (1997).
- [14] M.A. Gulgun and W.M. Kriven, *Ceramic Transactions*, J.J Kingsley, C.H. Schilling and J.H. Adair, Ed., Vol.62 (American Ceramic Society, Westerville, OH, 1996) p.57.
- [15] M.A. Gulgun, M.H. Nguyen and W.M. Kriven, *J.Am. Ceram. Soc.* (1996) submitted.
- [16] S.J. Lee and W.M. Kriven, *J.Am. Ceram. Soc.* (1997) submitted.
- [17] M.H. Nguyen and W.M. Kriven, *J. Am. Ceram. Soc.* (1997) submitted.
- [18] M. Pechini, U.S.Pat.No.3 330 697, July 11. (1967).
- [19] D. Budd and D.A. Payne, *Mater. Res. Soc. Symp. Proc.* 32 (1984) 239.
- [20] K. Toyoshima, *Polyvinyl Alcohol Properties and Applications*, C.A. Finch, Ed.,(John Wiley & Sons, New York, 1973) p.22.
- [21] Y. Takeuchi, *Mineral.J.* 2 (1958) 311.
- [22] W. Wong, H. McMurdie, B. Paretzkin, C. Hubbard and A. Dragoo, *Powder Diffraction.* 2 (1987) 107.
- [23] *CRC Handbook of Chemistry and Physics*, 50th ed., R.C. Weast, Ed.,(The Chemical Rubber Co., 1970).