ELSEVIER

Journal of Alloys and Compounds 234 (1996) 187–192

Journal of ALLOYS AND COMPOUNDS

Phase formation of BaB_2O_4 from melts in graphite crucible

H. Kimura[1], R.S. Feigelson

Center for Materials Research, Stanford University, Stanford, CA 94305-4045, USA

Received 29 May 1995; in final form 14 August 1995

Abstract

Conditions for formation of the low temperature β phase of BaB_2O_4 from nominally pure melts in graphite and Pt crucibles were investigated along with phase transformation kinetics. In order to obtain the β phase crystals from supercooled metastable melts in a graphite crucible, it was found necessary to first superheat the melts almost 100°C. The nucleation–growth behavior was different when a Pt crucible was used. This difference can be explained by the presence of graphite particles in the melts in the graphite crucible acting as nucleation sites. It was also found that bulk or powdered β phase crystals transformed to the high temperature α phase when heated for only 5 min above 1000°C (the equilibrium transformation temperature is 925°C). Some differences were found in the behavior of the β to α transformation of bulk and powdered crystals, and were believed related to thermal stress.

Keywords: Superheating; Supercooling; Metastable phase formation; Phase transformation

1. Introduction

The low temperature β phase crystal of BaB_2O_4 (BBO) is important for ultra violet nonlinear optical devices. BBO melts congruently at 1095°C, and the high temperature α phase normally forms first from stoichiometric melts. The phase transformation kinetics are believed to be slow enough, so that under certain conditions the β phase will not form on cooling to room temperature. Crystals of the β phase are usually grown from high temperature solutions (flux growth) [1–3], but recently they have been grown by the Czochralski method from nominally pure supercooled melts [4–6]. Some problems associated with the solution growth of β-BBO are flux inclusions, difficulties in controlling crystal length and slow growth rates. Meanwhile, in the Czochralski or the Bridgman method, much faster growth rates are possible and flux inclusions are eliminated. The difficulties encountered in the Czochralski growth of β-BBO have included seeding problems, controlling the crystal diameter and length, and preventing the transformation to α phase during the growth. The Bridgman method may be more convenient and useful for BBO growth. In order to grow the β phase crystals from stoichiometric melts, it is usually necessary to use melts which have been extensively supercooled [7]. Nicolas et al. [8] have reported that the nucleation of a metastable phase by supercooling can be affected by the degree of superheating of the melts. Therefore, it is important for the successful Czochralski or Bridgman growth of β-BBO to understand the effects of superheating and supercooling.

In this paper, we report on the effects of superheating and supercooling on the nucleation–growth behavior of the β phase from nominally pure stoichiometric melts, and on the kinetics of the β to α transformation (for bulk and powdered samples) in a graphite crucible in order to obtain β phase single crystals by the Bridgman method. The latter study involve annealing the β phase samples in the α phase stability temperature range.

2. Experimental procedures

BBO source material was produced by a solid state reaction using powders of $BaCO_3$ (Johnson-Matthey, 99.9%) and B_2O_3 (ALPHA, 99.9%). Table 1 shows the impurities found in the source material as measured by ICP mass spectroscopy. Zone refining was used to

[1] Present address: National Research Institute for Metals, 1-2-1 Sengen, Tsukuba, Ibaraki 305, Japan.

SSDI 0925-8388(95)02031-4

Table 1
Chemical concentrating of starting material C_s and that after ten zone refining operations C_f for BBO by ICP mass spectrometry: analysis in ppm

Elements	Al	Ca	Eu	La	Mg	Si	Sr	Y
C_s	42	378	71.1	6	18	83	641	4.7
C_f	16	269	67.1	5.7	12	61	493	3.6

purify the starting materials (up to ten passes), but the impurity level did not decrease very much. The starting materials used in the present work came from the zone refined crystals to assure the stoichiometry [9]. To make sure that only the β phase was present, all starting materials were annealed in an air atmosphere for 5 h at 900°C (below the transformation temperature of 925°C [10]). Bulk samples were obtained by breaking apart BBO boules. Powdered samples were obtained by grinding bulk crystals (the average particle diameter was 1.2 mm for the bulk samples and 0.04 mm for the powders). The bulk samples consisted of many fine grains.

R.f. induction heating was used to heat the graphite crucible (diameter 10 mm × 10 mm height) which was mounted in a quartz tube in a N_2 atmosphere. Heating was controlled using a PID controller by means of the open output power control method. Graphite does not react with BBO and is not wetted by BBO melts [11]. The temperature was measured at a point on the outside wall of the crucible by an optical pyrometer which had been calibrated with a chromel–alumel (CA) thermocouple inserted into the graphite crucible using a calibration curve between temperature by the optical pyrometer and that by the thermocouple. The error in the temperature measurement was estimated to be ± 5°C.

Phase formation from melts superheated to various temperatures above the melting temperature was studied using a rapid cooling method. First, five milligram powdered samples were heated in the r.f. furnace to 900°C and held for 10 min to obtain thermal homogeneity. The temperature was then increased to the range of 1100 to 1250°C within 1 min and soaked at each temperature for 10 min. Finally, the melts were cooled rapidly to room temperature by turning off the r.f. power. The phases formed in each sample were identified using powder X-ray diffraction (XRD). The solidification temperature was measured during the rapid cooling stage (700 K min^{-1}), using a CA thermocouple inserted into the graphite crucible, recording a recalescence in a chart as an exothermic peak. A steep peak was observed corresponding to the recalescence. In order to obtain the solidification temperature at slower cooling rates (10 K min^{-1}), differential thermal analysis (DTA) in an Ar atmosphere was carried out.

Five milligram samples were used to study the solid state phase transformation behavior. The samples were heated in the graphite crucible (diameter 10 mm × 10 mm height) from room temperature to 950, 1000, 1050 and 1090°C within 5 min (about 200 K min^{-1}) and then annealed for a period of time in the r.f. heating furnace. Individual samples were then rapidly cooled after 5, 15, 30 and 60 min by turning off the power. The phases generated were verified by powder XRD from 20 to 45° by 0.1° step scan using Cu K_α radiation. The mass% of each phase present in the sample was obtained by a peak intensity relationship between the (10$\underline{1}$0) of the α phase and the (113) of the β phase. Only these peaks were strong enough to enable more than 1000 counts by 0.1° to be obtained with no overlapping in the present experiments. To make sure of the amount of each phase, the peak intensity relationship was compared with that of standard samples having different α/β phase ratios. The experiments were carried out twice, and the values were averaged. The total absolute error in determining the mass% of each phase was estimated to be ± 15%; this included a maximum temperature error of ± 5°C, an XRD error of ± 5% and annealing time error of 1 min. The present error is enough to estimate the transformation behavior. Furthermore, the dependence of the β to α phase transformation on heating rate (1 to 40 K min^{-1}) in the range of 900 to 1050°C was studied in order to identify the solid phase present before melting (both for bulk and powdered samples) using five milligram samples in an r.f. heating furnace having a programmed controller. These samples were annealed for 5 min at 1000 or 1050°C in order to obtain a homogeneous temperature before rapid cooling.

3. Results and discussion

3.1. Melt crystallization

Table 2 shows the relationship between melt soak temperature T_h, solidification temperature T_s and the phases formed for two cooling rates and crucible materials. In the graphite crucible, the β phase formed above the equilibrium β to α phase transformation temperature (925°C) when the melt was superheated above 1197°C. Dependence on the cooling rates was not observed. Meanwhile, in the Pt crucible, much larger supercooling (below 925°C) occurred before solidification took place. The β phase formed in the Pt crucible even for a melt temperature as low as 1124°C. This kind of result in a Pt crucible was also found by Voronko et al. [12] in Raman spectral analysis of BBO melts. In our experiments, the α phase only formed from melts held in a Pt crucible at 1170°C when the melts were contaminated by graphite par-

Table 2
Relationship between melt soak temperature T_h, solidification temperature T_s, and the phases formed at two cooling rates and crucible materials (RF: induction heating furnace, DTA: DTA furnace, G: graphite crucible and Pt:Pt crucible)

Cooling rate (K min^{-1})	Crucible	Furnace	T_h (°C)	T_s (°C)	Phase
700	G	RF	1247	1014	β
			1221	1081	β
			1197	1037	β
			1150	1076	α
10	G	DTA	1250	1019	β
			1211	1003	β
			1153	1014	α
10	Pt	DTA	1203	833	β
			1176	822	β
			1170[1]	989[1]	α
			1124	807	β

[1] Results for sample containing graphite particles.

ticles. This suggests that graphite acts as a nucleation site and plays an important role in determining which phase is formed at a specific melt temperature.

In general, the rate of nucleation (I_i) as a function of solidification temperature T_s can be expressed as follows [7,13]:

$$I_i = K \exp[-G_i^* f(\theta_i)/kT] \quad (1)$$

Here

$$G_i^* = 16\pi(\sigma_i^3/G_i^2)/3 \quad (2)$$

$$f(\theta_i) = (2 + \cos\theta_i)(1 - \cos\theta_i)^2/4 \quad (3)$$

$$G_i = L_i(\Delta T_i)/T_m \quad (4)$$

where K is a kinematic parameter involving dynamic viscosity, θ_i is the contact angle between the melt and the solid crystallized as heterogeneous nucleation, k is the Boltzmann constant, σ_i is the apparent surface energy of melt, L_i is the latent heat of solidification, ΔT_i is the supercooling temperature, and T_m is the melting temperature. ΔT_i values are different for graphite and Pt crucibles. It is assumed that nucleation occurs at roughly the same I_i value for both graphite and Pt crucibles, and values of the contact angle θ_i' between the melt and the crucible can be used as those of the contact angle θ_i. Therefore, if the ratio of latent heat in the graphite to the Pt crucibles (L_G/L_{Pt}) is unity, the ratio of surface energy (σ_G/σ_{Pt}) is estimated to be 0.1 from Eqs.(1)–(4), using the contact angles measured by Katsumata et al. ($\theta_G' = 78°$ and $\theta_{Pt}' = 22°$) [11]. This value is reasonable for the decrease in surface energy caused by an impurity or an inclusion. Consequently, the difference in surface energy may determine the nucleation–growth behavior in BBO melts.

3.2. Solid state phase transformation

Fig. 1 shows the annealing time–temperature dependence for the solid state β to α transformation for bulk (Fig. 1(a)) and powdered samples (Fig. 1(b)). The α phase was the only phase found in the bulk samples heated above 1050°C, while in the powdered samples, a mixture of the β and α phase was obtained even at 1050°C. The reason for this difference in obtained phases was the thermal stress during heating. The effect of the thermal stress during rapid cooling can be ignored because, compared with heating, on cooling the stable low temperature (β) phase is formed. Knowledge of this phase transformation behavior is important, not only for determining the optimum cooling rate necessary for crystal growth from pure melts by the Czochralski or the Bridgman method, but also for preventing the β phase seeds from transforming to the α phase during heating. Unless an adequate cooling rate is used, the β phase crystal which is nucleated as a metastable phase may transform to the α phase during the growth process in the α phase

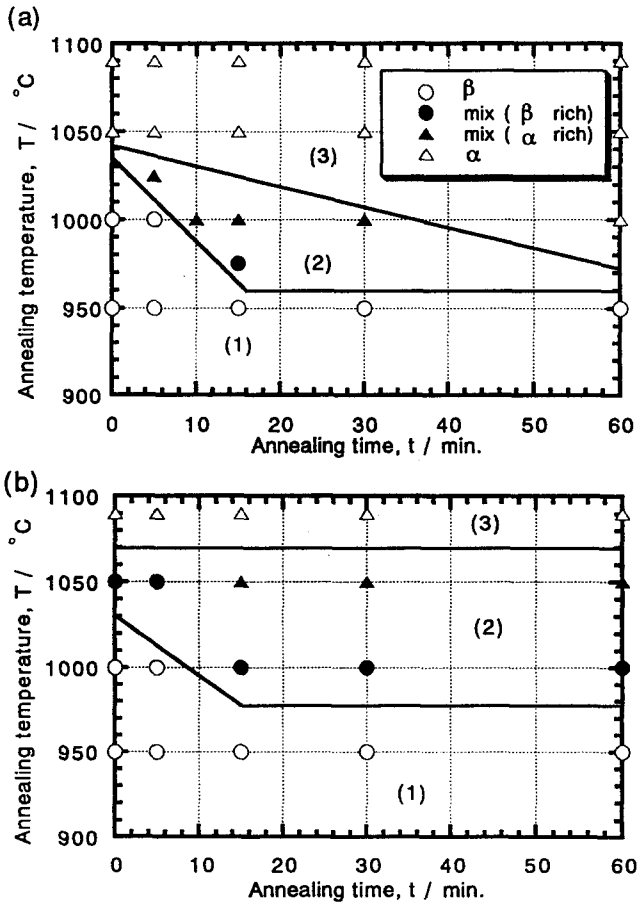

Fig. 1. Annealing time–temperature dependence for β to α phase transformation at several different annealing temperatures for (a) bulk, and (b) powdered samples. The chart is divided into the three phase regions obtained: (1) β, (2) $\beta + \alpha$ and (3) α.

stability region. Fig. 1 is divided into three regions where β, $\beta + \alpha$ and α phases are formed. From Fig. 1(a) for the bulk samples, the cooling rate necessary to prevent the β phase crystal from transforming to α in the α stability temperature range must be larger than 5 K min^{-1}. Here the cooling is estimated to start at 1030°C because this is the average solidification temperature obtained in the experiments described in Table 2.

Table 3 shows the relationship between the phases formed at different cooling rates from the melts initially held at 1250°C in a graphite crucible. The crystals with cooling rates of 10 and 5 K min^{-1} contained only the β phase but at rate of 0.9 K min^{-1} had both the β and the α phases. This is in good agreement with the annealing behavior for the β phase bulk crystals as shown in Fig. 1(a). This rate is large compared with normal cooling rates of oxide single crystals after growth in the Czochralski method (50–100 K h^{-1}). However, from both the growth rate of β-BBO of 0.08 mm min^{-1} [14] and the required cooling rate of 5 K min^{-1}, the temperature gradient at the growth front is estimated to be 62.5 K mm^{-1}, which is in agreement with the value of 50–100 K mm^{-1} in the successful β-BBO growth.

Fig. 2 shows the α/β phase ratio of transformed β phase crystals as a function of annealing time (obtained from XRD peak intensities). The α phase crystals already formed during the heating process up to 1050°C, while a negligibly small induction period was observed for both the bulk and the powdered samples heated at 1000°C. This transformation followed a Toschev nucleation model [15].

$$x = 1 - \exp[-I_0(t - t_0)] \quad (5)$$

where x is the α/β phase ratio, I_0 is the nucleation rate of the α phase, t is the time, and t_0 is the induction period. Powders annealed at 1000°C did not transform completely to the α phase within the annealing times used in these experiments, i.e. they required longer annealing times to complete the transformation. This not only suggests that thermal activation energy is necessary for the β to α transformation at 1000°C, but that thermal stress plays an important role.

Fig. 3 shows a heating rate dependence of the α/β phase ratio transformed during the annealing of the β phase crystals up to 1000°C for the bulk and up to 1050°C for the powdered samples. It is difficult to retain the β phase before melting, even though a slow heating rate is used, so that the raw material for the usual single crystal growth melts from the α phase. In Fig. 3, a logarithmic relationship was found between

Table 3
Crystal phases formed at different cooling rates from melts at 1250°C in a graphite crucible

Cooling rate (K min^{-1})	10	5	0.9
Crystal phase	β	β	$\beta + \alpha$

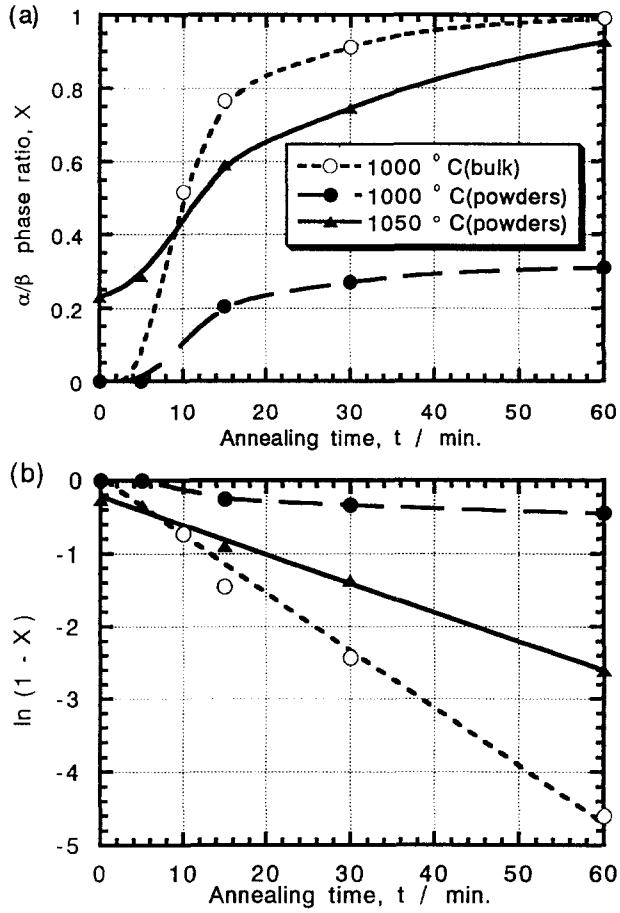

Fig. 2. Time dependence of α/β phase ratio transformed obtained by XRD peak intensity in Fig. 1. (a) Normal plot, and (b) logarithmic plot, heated at 1000°C for bulk, and 1000 and 1050°C for powders. Numerical relationships are obtained as shown in the following, except for powders heated at 1000°C. x is α/β phase ratio and t is time in min. $x = 1 - \exp[-4.0 \times 10^{-2}(t + 5)]$ (1050°C, powders), $x = 1 - \exp[-7.9 \times 10^{-2}(t - 0.6)]$ (1000°C, bulk).

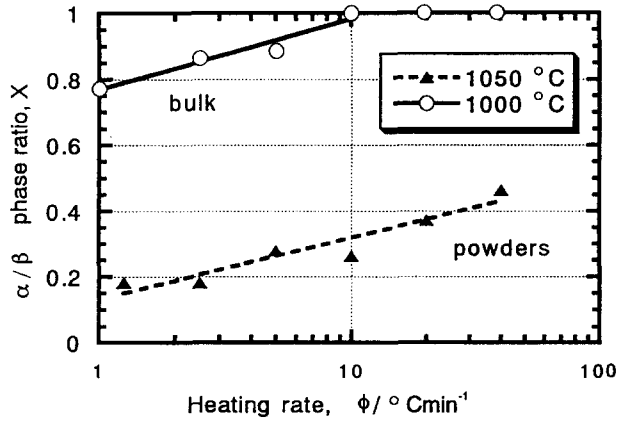

Fig. 3. Heating rate dependence of α/β phase ratio caused by β to α phase transformation heated up to 1000°C for bulk and 1050°C for powders.

the α/β phase ratio and the heating rate in both samples. The slower the heating rate is, the more the β phase remains. The difference in transformation behavior between the bulk and the powdered samples appears, therefore, to be due to thermal stress generated during the heating process.

Generally, thermal stress σ_s at the surface of solids during heating can be denoted by Eq. (6) assuming a parabolic shape thermal profile in the crystal [16]

$$\sigma_s = \left(\frac{Ea}{1-\mu}\frac{1}{\lambda/\rho C_p}\right) F_g \phi r_m^2 \quad (6)$$

where E is Young's modulus, a is the linear expansion coefficient, μ is Poisson's ratio, λ is the thermal conductivity, ρ is the density, C_p is the heat capacity, F_g is a geometrical factor, ϕ is the heating rate and r_m is the half thickness of the crystal. Assuming a cubic crystal shape, F_g is 0.221. From Fig. 3, a ϕ(powders)/ϕ(bulk) ratio of 860 is obtained for the case when the β to α transformation does not occur, i.e. the heating rate for which the α/β phase ratio is zero. In addition, an $[r_m(\text{powders})/r_m(\text{bulk})]^2$ ratio of 1/900 is obtained at 0.02 mm of r_m(powders) and 0.6 mm of r_m(bulk). Therefore, the β to α transformation in the bulk and the powdered samples begins at similar thermal stress according to Eq. (6).

For the Clausius–Clapeyron relationship, the following equation can be applied:

$$dT/dp = T(v_\beta - v_\alpha)/q \quad (7)$$

where T is the temperature, p is the pressure, q is the latent heat of the transformation, and v_β and v_α are the mole volumes of each phase. It is difficult to measure the value of q, even using differential scanning calorimetry, i.e. q is expected to be small, so that large dT/dp is expected. Therefore, the thermal stress dependence of the transformation is reasonable. Furthermore, the tensile and compressive components of the thermal stress are comparable for the transformation [17].

The difference in the transformation ratio observed in Figs. 2 and 3 is mainly caused by an effect on the cause of the transformation, i.e. by the thermal stress or by a thermal activation process. The transformation is dependent on the heating rate, balancing between the effect of the thermal stress and that of the thermal activation process. Furthermore, because of the rapid transformation, the experimental error becomes large at the annealing time from 0 to 10 min in Fig. 2. Therefore, it is difficult to compare the ratio in Fig. 2 with that in Fig. 3 which has a different thermal history. However, for the purposes of this experiment, these results are enough to know the phase before melting.

From the above results, it is difficult to retain the β phase crystal just before melting, so that just after melting an α phase structure is expected to be present. Of course, the present melt crystallization experiments are affected by the transformation, but 10 min holding time of melt is expected to be enough to relax the α phase structure in the melt.

4. Summary

The conditions for the formation of the β or α phases of BBO in graphite and Pt crucibles were investigated. For rapid (700 K min^{-1}) or slow (10 K min^{-1}) cooling rates, the β phase crystals could be obtained only from melts heated above 1197°C. The α phase crystal was only obtained from melts heated below 1150°C. The β phase, therefore, formed as a metastable phase in melts superheated almost 100°C when a graphite crucible was used. The nucleation–growth behaviors in graphite and Pt crucibles were different. This difference could be explained by the decrease in surface energy associated with graphite particles on the melt surface. During annealing in a graphite crucible, the β phase crystals in the α phase temperature range (above 925°C) will rapidly transform to the α phase. The cooling rate necessary to obtain the β phase crystals from the melts (suppressing the β to α phase transformation) must be larger than 5 K min^{-1}. Therefore, superheating by almost 100°C and rapid cooling above 5 K min^{-1} is required for the Bridgman method to obtain the β phase single crystal.

Acknowledgements

This work was supported by the National Science Foundation through the Center for Materials Research, Stanford University. We thank Dr. R.K. Route for helpful discussions, and Dr. Y. Kaieda and Mr. N. Oguro of the National Research Institute for Metals for measuring powder diameters. One of the authors (H.K.) was granted Santo Funds to study abroad by the Foundation of Tsukuba EXPO'85 in Japan.

References

[1] R.O. Hengel and F. Fischer, *J. Cryst. Growth, 114* (1991) 656.
[2] D.Y. Tang, R.K. Route and R.S. Feigelson, *J. Cryst. Growth, 91* (1988) 81.
[3] P.F. Bordui, G.D. Calvert and R. Blachman, *J. Cryst. Growth, 129* (1993) 371.
[4] K. Itoh, F. Marumo and Y. Kuwano, *J. Cryst. Growth, 106* (1990) 728.
[5] H. Kouta, Y. Kuwano, K. Ito and F. Marumo, *J. Cryst. Growth, 114* (1991) 676.
[6] Y. Kozuki and M. Itoh, *J. Cryst. Growth, 114* (1991) 683.

[7] B. Feuerbacher, *Mater. Sci. Rep.*, *4* (1989) 1.
[8] J. Nicolas, J. Coutures, J.P. Coutures and B. Boudot, *J. Solid State Chem.*, *52* (1984) 101.
[9] T. Katsumata, H. Ishijima, T. Sugano, M. Yamagishi and K. Takahashi, *J. Cryst. Growth*, *123* (1992) 597.
[10] K.H. Hubner, *Neues Jahrb. Miner. Monatsh.*, (1969) 335.
[11] T. Katsumata, K. Ohshima, K. One, M. Hisamoto, T. Ohtaki, H. Konoura, H. Nakagawa and K. Takahashi, *J. Cryst. Growth*, *125* (1992) 270.
[12] Y.K. Voronko, A.V. Gorbachev, V.V. Oshiko, A.A. Sobol, R.S. Feigelson and R.K. Route, *J. Phys. Chem. Solids*, *54* (1993) 1579.
[13] D. Turnbull, *J. Chem. Phys.*, *20* (1952) 411.
[14] H. Kimura, T. Numazawa and M. Sato, submitted to *J. Cryst. Growth.*
[15] S. Toschev, A. Milchev and S. Stoyanov, *J. Cryst. Growth*, *13–14* (1972) 3.
[16] W.D. Kingery, H.K. Bowen and D.R. Uhlmann, in *Introduction to Ceramics*, Wiley, 1976, 2nd edn., p. 816.
[17] M. Umemoto, in Jpn. Soc. Mech. Eng. (ed.), *Thermomechanical Behavior of Materials during Transformation—Theory and Numerical Simulation*, Corona, Tokyo, 1991, p. 31 (in Japanese).