Ceramics International 30 (2004) 509–514

CERAMICS
INTERNATIONAL

www.elsevier.com/locate/ceramint

Effect of microwave processing on polymorphic transformation of TiO_2

S.A. Borkar, S.R. Dharwadkar*

Department of Chemistry, The Institute of Science, 15, Madam Cama Road, Mumbai 400032, India

Received 26 November 2002; received in revised form 27 June 2003; accepted 1 September 2003

Abstract

Microwave (MW) processing for ceramics is gaining attention all over the world due to its inherent advantages. In this paper, we have attempted to examine the influence of microwave heating on polymorphic phase transformation of titanium dioxide from anatase to rutile. The results are compared with those obtained by heating the same samples in resistance heated furnace under identical conditions. The study indicated that in the microwave heating, complete transformation of pure anatase phase to rutile takes place at lower temperature (900 °C, 30 min dwell time) compared to only partial conversion (<60%) to rutile when the same sample is heated in conventional resistance furnace at 1000 °C for 30 min. The results obtained further show that the presence of rutile phase in the anatase sample considerably accelerates its transformation to rutile irrespective of the mode of heating (i.e. microwave or resistance heating) adopted in the experiment.

Keywords: A. Microwave processing; D. TiO_2; Polymorphic transformation

1. Introduction

Microwaves (MW) in recent years are being explored as an efficient alternate energy source in material processing. Microwave heating offers number of advantages over the conventional resistance heating process [1–3]. A number of studies on the microwave assisted processes in different ceramic systems were reviewed by Sutton [2]. There are however, hardly any investigations in which the influence of the microwave on purely polymorphic transformations have been studied. The effect of microwave heating on TiO_2 pellets was reported by Ikuma [4]. These authors observed that during microwave heating in a single mode cavity, 100–250 °C difference in temperature existed between the bulk and the surface of the cylindrical pellets. Maximum conversion of about 25 mol% of anatase to rutile was reported in the middle of the pellet when the surface temperature was of the order of 760–860 °C. Plazl et al. [5] studied the anatase to rutile transformation in anatase gels using specially designed high-pressure microwave reactor connected to the commercial microwave oven. They reported 92.4% phase transformation of anatase to rutile when the gels mixed with carbon in the proportions of anatase to carbon 3:1 and 2:1 were heated in the microwave oven at 1000 °C. They observed considerable enhancement in the rate of transformation of anatase to rutile when the microwave heating was employed. However, the extent to which microwaves alone affect the rate of transformation is difficult to conclude, since they have used the mixture of anatase gel and carbon in their experiments. In this paper we report the results obtained on the phase transformation in TiO_2 samples prepared in our laboratory from $Ti(OH)_4$ precursor, on heating in microwave system and conventional resistance heated furnace.

It is known that for different applications of TiO_2, careful tailoring of powder properties such as phase composition, surface area, particle morphology is needed. In titania system, amorphous to crystalline transformation and polymorphic phase transition depend on the temperature of heat treatment. The poorly crystalline oxide prepared at low temperature crystallizes progressively to ‘anatase phase’ with the increasing temperature, which on further heating transforms irreversibly to a thermodynamically stable rutile phase. The anatase to rutile transformation in TiO_2 is known to be influenced by several experimental conditions including the method of synthesis of the parent oxide [6]. In this paper, the polymorphic transformation in TiO_2 prepared by two different chemical routes is studied

---

* Corresponding author. Tel.: +91-900-022-282-9293x350.
E-mail address: srdharwadkar@hotmail.com (S.R. Dharwadkar).

0272-8842/$30.00
doi:10.1016/j.ceramint.2003.09.004

by employing microwave and conventional heating methods. The results obtained clearly demonstrate that, both the rate of conversion as well as the percentage conversion of anatase to rutile depends on the type of process employed for the precursor preparation and the type of heating.

2. Experimental

2.1. Preparation of titania precursor

In the present study, two different processes were employed to prepare TiO_2 from dilute $TiCl_4$ (Merck, Synthesis grade with purity >99%) solution. The TiO_2 samples were prepared from $Ti(OH)_4$ precursors by Controlled Precipitation and Hydrolysis Process.

2.1.1. Controlled precipitation process

In controlled precipitation process, dilute $TiCl_4$ solution was mixed with urea solution in proportion of TiO_2:urea concentration 1:20 mol. The reaction mixture was then heated at ∼100 °C and refluxed for 2–3 h. The resulting reaction mass was cooled and filtered. The precipitate was washed several times with hot demineralized water till it was free of chloride ions.

2.1.2. Precipitation by hydrolysis

In hydrolysis process, the hydroxide precursor was prepared as described in Ref. [6] with minor modification. In this process, the stock solution of $TiCl_4$ was further diluted five to six times with demineralized water. The solution was refluxed at 100 °C for 3 h and cooled to room temperature. The supernatant liquid from settled precipitate was removed carefully by siphoning. Fresh demineralized water was added to the residual precipitate and mixed thoroughly to form consistent slurry. To the slurry, dilute ammonia was added drop wise under stirring condition till the slurry became neutral, i.e. pH ≅ 7. The precipitate so obtained was filtered and washed with demineralized water till free of chloride ions.

2.1.3. Precursor treatment

The hydroxide precipitates obtained by both the methods were vacuum dried at room temperature. The dried powder were ground in agate-mortar and sieved through 200 mesh sieve.

The powders obtained by both the above methods were heated in the in-house developed microwave system [7] as well as tubular resistance furnace independently at 300 °C for 1 h. The two lots thus prepared were stored in desiccators for further use.

The powders prepared at 300 °C were heated further at different temperatures ranging from 500 to 1000 °C at an interval of 100 °C. The dwell time for the sample at each temperature was 30 min. Equal weights of the samples were heated in microwave system and conventionally heated resistance furnace under identical conditions employing similar type of sample holder. Experiment at each temperature was repeated thrice under identical experimental conditions.

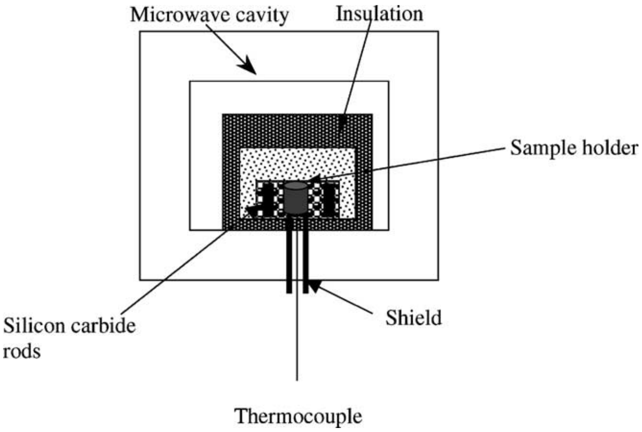

Fig. 1. Schematic diagram of microwave system.

Fig. 1 shows the schematic diagram of the microwave system used in the present investigation. The unit consists of magnetron operating at 2.45 GHz with adjustable power settings and full power level of 750 W. The temperature of the sample was controlled within ±3 °C of the set value through an on/off temperature controller coupled to the magnetron input power source. Calibrated Pt, Pt–13%Rh shielded thermocouple was used for measurement of sample temperature. To avoid sparking, the shield of thermocouple was grounded and to obtain precise sample temperature, the tip of the thermocouple was embedded within the powder sample (weighing ∼2–3 g). The samples were kept in a well insulated sample holder carved from mullite fiber boards. The sample holder was surrounded by four silicon carbide rods located symmetrically around the sample holder. These rods act as pre-heaters [8] for the sample under investigation.

The resistance heated furnace consisted of a Kanthal wire wound tubular furnace. The temperature of the sample in this case was measured with the calibrated chromel–alumel thermocouple and controlled within ±2 °C of the set value.

The samples after heat treatment were mixed thoroughly in the agate mortar and sieved through 300 mesh sieve. The total sample was divided in to three parts and all three were analyzed for phase composition.

2.2. Characterization of TiO_2 powders prepared by two different methods

The powders heated by microwave and conventional heating methods were passed through 300 mesh and characterized by X-ray diffraction technique using Cu Kα radiation using Phillips X'Pert X-ray diffractometer. The weight fraction "alpha" of rutile in TiO_2 in different samples was calculated using the following equation [9].

$$\alpha = \frac{1}{1 + 0.884(A_{\text{anatase}}/A_{\text{rutile}})} \tag{1}$$

where '$A_{anatase}$' and 'A_{rutile}' represent respectively the integral intensities of anatase peak (1 0 1), i.e. at 2θ value of 25.4° and rutile peak (1 1 0) at 2θ value of 27.5°. 'α' is the extent of the transformation of anatase, i.e. weight fraction of rutile in the mixture.

3. Results and discussion

The TiO_2 obtained by controlled precipitation method consisted of a single anatase phase while that obtained by hydrolysis process consisted of a mixture of anatase and rutile. It was interesting to study progress of phase transformation for the sample containing only pure anatase and the one in which anatase co-existed with the rutile phase. The comparative studies were done by heating samples in microwave system as well as in conventional resistance heated furnace for the same duration. The average weight fractions of rutile (α) calculated for different samples from the XRD patterns (obtained by averaging α value of three sub-samples) using Eq. (1) are listed in Table 1.

3.1. Effect of type of heating on polymorphic transformation in TiO_2

3.1.1. TiO_2 obtained from the precursor prepared by controlled precipitation

The X-ray powder diffraction patterns of TiO_2 sample obtained by heating $Ti(OH)_4$ precursor prepared by controlled precipitation process, recorded in the range 24–29° 2θ, are shown in Figs. 2 and 3. Fig. 2 shows the X-ray diffraction patterns of TiO_2 heated in resistance furnace to different increasing temperatures. The XRD patterns presented in Fig. 3 are those of TiO_2 sample from the same batch heated in the microwave system at different temperatures. The pattern for the sample prepared by heating the $Ti(OH)_4$ precursor at 300 °C consisted of a single broad peak around 25.4° 2θ corresponding to (1 0 1) plane in the anatase phase. This sample on heating above 500 °C, progressively improved in crystallinity and got converted to the rutile phase (Figs. 2 and 3) above 600 °C. The conversion of anatase to rutile resulted in appearance of the peak around 27.5° 2θ corresponding to (1 1 0) plane of the rutile phase. The intensity of this peak increased progressively with the increasing temperature.

The increase in sharpness of the peaks with temperature rise between 300 and 700 °C in Fig. 2 suggests that the material is becoming more and more crystalline with increasing temperature. The decrease in intensity of the anatase peak and the simultaneous increase in the intensity of the rutile peak with the increasing temperature observed in Fig. 2 indicates progressive increase of the rutile phase with the increasing temperature.

The percentage of the rutile phase formed by heating the same amount of the anatase sample at different temperatures in resistance furnace and microwave system for the same dwell time of 30 min was calculated using Eq. (1) and is listed in Table 1 (columns 2 and 3). The weight fraction of rutile formed from the parent anatase phase, on heating it to different temperatures in the resistance furnace and microwave heating system is presented in graphical form in Fig. 4. The results presented in Fig. 4 and Table 1 indicate that the rate of conversion of anatase to rutile is marginally

Table 1
Weight fraction of rutile calculated from XRD patterns[a]

	Controlled precipitation (urea)		Hydrolysis (dilution)	
	Furnace	MW	Furnace	MW
500 °C, 30 min	0	0	0.56	0.68
600 °C, 30 min	0	0	0.60	0.69
700 °C, 30 min	0.03	0.01	0.86	0.90
800 °C, 30 min	0.17	0.86	1.00	1.00
900 °C, 30 min	0.49	0.99	–	–
1000 °C, 30 min	0.58	–	–	–

[a] The data presented is average of three experiments conducted on the samples from the same lot.

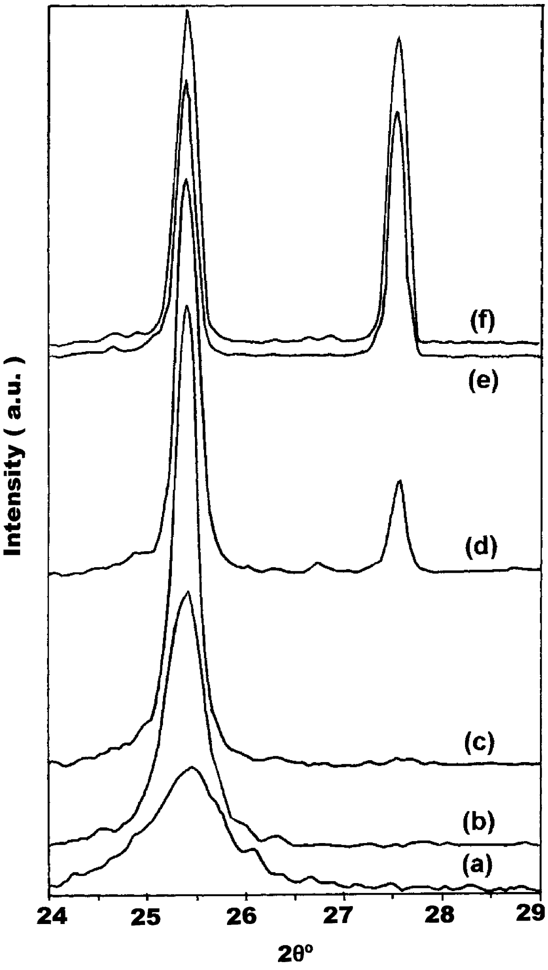

Fig. 2. Polymorphic transformation of anatase prepared by controlled precipitation method to rutile heated in resistance furnace. (a) 300 °C, (b) 500 °C, (c) 600 °C, (d) 800 °C, (e) 900 °C, (f) 1000 °C.

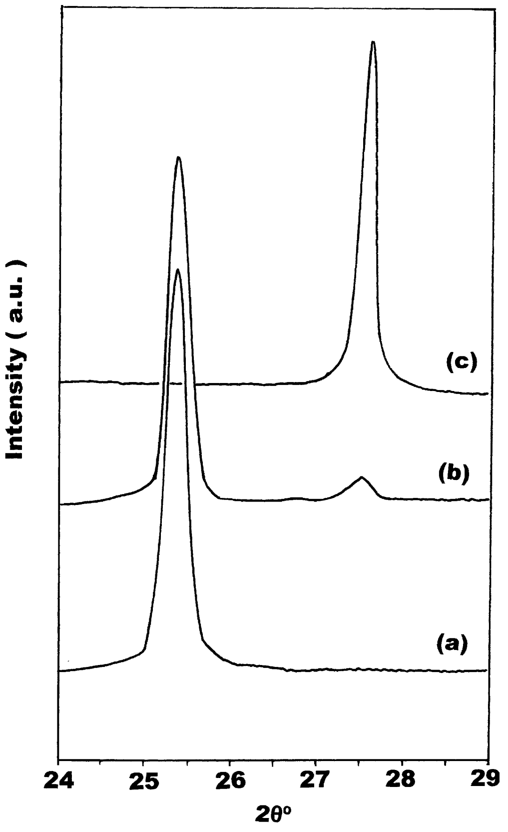

Fig. 3. Polymorphic transformation of anatase prepared by controlled precipitation method to rutile heated in microwave system. (a) 300 °C, (b) 800 °C, (c) 900 °C.

higher for the sample heated in the resistance below 800 °C Fig. 4a. However, above 800 °C the rate of conversion in microwave system is remarkably higher and the conversion to rutile is virtually complete by 900 °C Fig. 4b. The anatase sample heated in the resistance furnace converted to rutile only to the extent of 50% at 900 °C Fig. 4a. The rate of conversion reduced considerably above this temperature, reaching about 58% at 1000 °C.

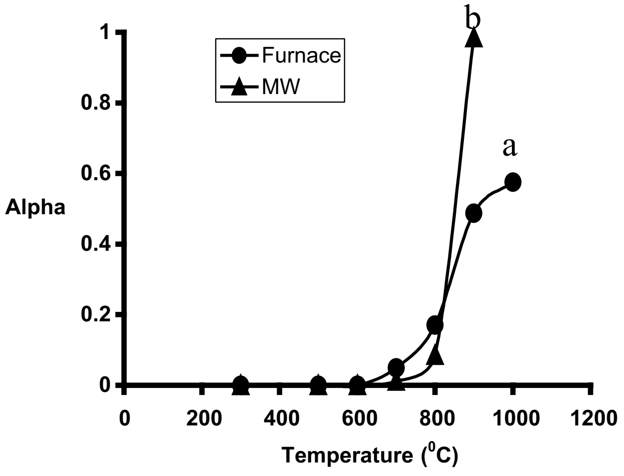

Fig. 4. Percent conversion of anatase (prepared by controlled precipitation method) to rutile in furnace (a) and microwave (b).

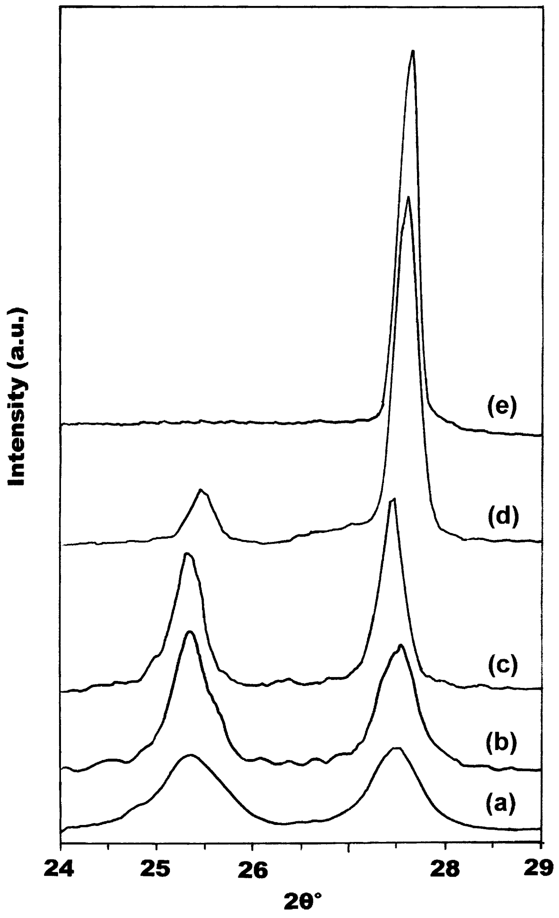

Fig. 5. Polymorphic transformation of anatase (in the mixed phase) prepared by hydrolysis method to rutile, heated in resistance furnace. (a) 300 °C, (b) 500 °C, (c) 600 °C, (d) 700 °C, (e) 800 °C.

3.1.2. TiO_2 obtained from precursors prepared by hydrolysis process

The $Ti(OH)_4$ precursor obtained by hydrolysis process when heated at 300 °C for 1 h yielded the mixture of anatase and rutile. The X-ray diffraction pattern recorded for this mixture is shown in Fig. 5. Heating this mixture to higher temperatures in the range 600–800 °C in the resistance furnace showed progressive decrease of the anatase phase in the mixture with the increasing temperature. The anatase in the mixture transformed completely to rutile on heating the sample for 30 min and at 800 °C in the resistance furnace. The extent of conversion of anatase in the mixture to rutile for the dwell time of 30 min at different temperatures is presented in Table 1 (column 4). The results of microwave processing of the sample obtained by hydrolysis process, presented in Table 1 (column 5) indicate that the conversion rate of anatase to rutile was marginally higher in furnace heated samples (Fig. 6a), but it was nearly complete at 800 °C in both the cases (Fig. 6; Table 1).

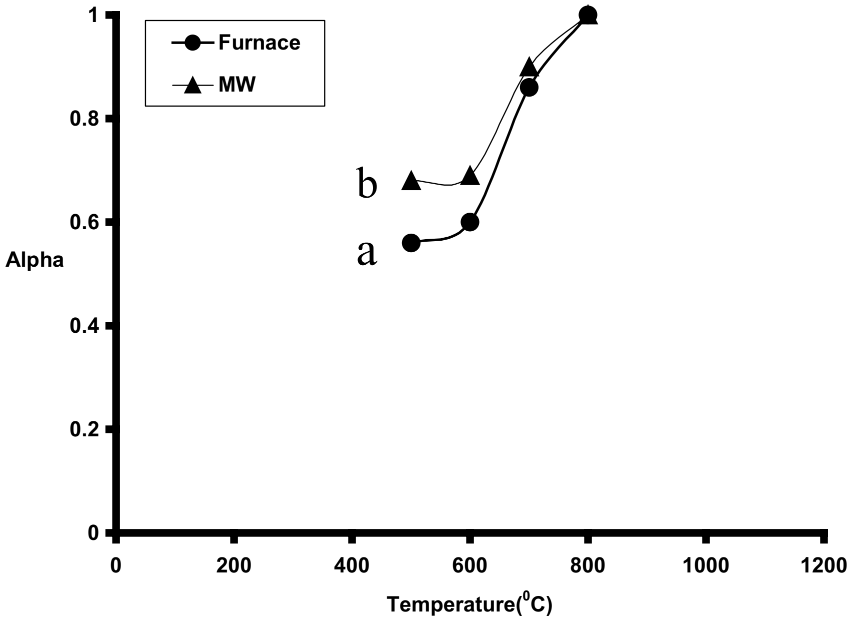

Fig. 6. Percent conversion of anatase in the mixture (prepared by dilution process) to rutile in furnace (a) and microwave (b).

4. Conclusions

1. The results presented above revealed that TiO_2 obtained from $Ti(OH)_4$ precursor prepared by controlled precipitation and hydrolysis methods differ in their phase composition. The powder obtained by controlled precipitation consisted of a single anatase phase while that obtained by dilution process indicated almost equal proportions of anatase and rutile phase, under the conditions employed in the present study.
2. Initially at low temperatures, the anatase to rutile phase transformation rate was marginally higher in the resistance furnace heated samples. However, these samples when heated further in the resistance furnace up to 1000 °C for 30 min, transformed to rutile only to the extent of 58% (Fig. 4a). The same sample when heated in microwave system, converted completely to rutile at 900 °C with the same dwell time of 30 min (Fig. 4b).
3. The anatase in the mixture transformed completely to rutile by about 800 °C irrespective of the mode of heating employed (Fig. 6).

All the foregoing observations suggest that

(a) The in situ rapid generation of heat in the microwave heating promotes rapid phase transition in pure anatase.
(b) The rate of in situ heat generation in the (anatase + rutile) mixture is relatively low, perhaps due to poorer microwave absorbing capacity of the co-existing rutile phase [10] and the rate of heating of the mixture in the microwave as well as resistance heated furnace is nearly identical, thereby yielding almost same rate of conversion in the two cases.
(c) The mixture however transforms completely to rutile by about 800 °C, a temperature which was 100 °C lower than that required for the transformation of the pure anatase phase (Fig. 4b). This effect is observed irrespective of the mode of heating employed and could perhaps be due to the catalytic effect of the co-existence of the rutile phase in the mixture [5].

References

[1] R. Roy, D. Agrawal, J.P. Cheng, M. Mathis, MW processing: triumph of applications-driven science in WC-composites and ferroic titanates, microwaves: theory and application in materials processing IV, in: Proceedings of First World Congress on Microwave Processing, Ceramic Transactions, Am. Ceram. Soc. 80 (1997) 3–26.
[2] W. Sutton, MW processing of ceramic materials, Am. Ceram. Soc. Bull. 68 (2) (1998) 376–386.
[3] S.B. Bahaduri, W.R. Tinga, J.G. Huang, E.H. Zhou, S. Bhaduri, Auto ignition synthesis & MW sintering of nano-crystalline ceramics, microwaves: theory and application in materials processing V, in: Proceedings of Second World Congress on Microwave Processing, Ceramic Transactions, Am. Ceram. Soc. 111 (2000) 181–188.
[4] Y. Ikuma, T. Shigemura, T. Hirose, J. Am. Ceram. Soc. 79 (10) (1996) 2533–2538.
[5] I. Plazl, D. Ravnjak, T. Koloini, A. Lubej, Microwaves: theory and application in materials processing V, in: Proceedings of Second World Congress on Microwave Processing, Ceramic Transactions, Am. Ceram. Soc. 111 (2000) 207–213.
[6] S.-J. Kim, S.-D. Park, Y.H. Jeong, Homogeneous precipitation of TiO_2 ultra fine powders from aqueous $TiOCl_2$ solution, J. Am. Ceram. Soc. 82 (4) (1999) 927–932.

[7] S.A. Borkar, S.A. Khadilkar, B.K. Guptarishi, R.M. Cursetji, Microwave processing—a technological option for the future, in: International Seminar on Cement & Concrete, VIth NCBM, November 1998, vol. 3, pp. IX, 44–55.

[8] R. Roy, D. Agrawal, J. Cheng, S. Gedevanishvill, Nature 399 (1999) 668.

[9] H. Zhang, J.F. Banfield, Phase transformation of nano-crystalline anatase to rutile via combined interface and surface nucleation, J. Mater. Res. 15 (2) (2000) 437–448.

[10] R.D. Peelamedu, R. Roy, D. Agrawal, Mater. Res. Bull. 36 (2001) 2723–2739.