4

Microwave Sintering of Thermistor Ceramics

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1. Introduction

Microwave sintering is a new sintering technology developed in the middle to late period of the 1980's, which is characterized by fast densification for ceramic materials[1]. In recent years, microwave heating has been well employed in the field of sintering and joining of ceramics as a result of its advantages against conventional methods. These ceramic materials include oxides, mixed oxides, non-oxides, composite ceramics, etc[2]. In addition, because ceramics have low thermal conductivities and are processed at high temperatures, many researchers have attempted to take advantage of volumetric heating for sintering, chemical vapor infiltration (CVI), and pyrolysis of polymeric precursors[3]. Now it has been found that the microwave sintering can also be applied as efficiently and effectively to thermistor ceramics as well as many other ceramics. This chapter compares advantages of microwave sintering with conventional sintering and presents some applications in thermistor ceramics.

2. Theoretical aspects of microwave sintering

Microwave is the name given to electromagnetic radiation 1 m to 1 mm in wavelength that corresponds to a frequency of about 300MHz to 300 GHz. Microwave heating is a process in which the materials couple with microwaves, absorb the electromagnetic energy volumetrically, and transform into heat. This is different from conventional methods where heat is transferred between objects by the mechanisms of conduction, radiation and convection[4]. In conventional heating, the material's surface is first heated followed by the heat moving inward. This means that there is a temperature gradient from the surface to the inside. However, microwave heating generates heat within the material first and then heats the entire volume[5].

2.1 The principle of microwave sintering

Microwave sintering makes use of dielectric loss of materials in microwave electromagnetic fields to heat ceramic matrix to the sintering temperature fast. The microwave sintering effect mainly comes from the continuous changes of material polarization in alternating electromagnetic field. The continuous changes of dipoles in materials can produce strong vibration and friction, therefore, generating heat to achieve sintering[1].

2.2 Advantages of microwave sintering comparison to conventional methods

Microwave sintering has achieved worldwide acceptance due to its significant advantages against conventional sintering methods, especially in ceramic materials. A summary of these are[2, 4]: (1) The observation of more rapid reaction and/or sintering during microwave processing of ceramics had led to speculation that microwave processing results in enhanced diffusion; (2) Since microwaves penetrate the dielectric with absorption and heat generation throughout the work piece, microwave sintering is much more efficient and lower processing costs;(3)Generally higher density and better grain distribution can be achieved through microwave sintering;(4) Microwave sintering can significantly shorten the sintering time leading to consume much lower energy than conventional sintering.

3. Application of microwave sintering in thermistor ceramics

Microwave sintering is a new sintering technology which can densify ceramic materials at a very rapid rate and at a substantially lower temperature than the conventional sintering process[6]. The following demonstrates microwave sintering advantages against conventional sintering for some oxide thermistor ceramics, including NTC thermistor ceramics and PTC thermistor ceramics.

3.1 Microwave sintering of NTC thermistor ceramics

Because of integrity and uniformity of microwave heating, the NTC thermistors of depending on uniformity and densification may show uniform microstructure during microwave sintering. A dense microstructure is necessary to obtain a good reproducibility of the electrical characteristics of the ceramic[7]. During microwave sintering, in addition to heating, the rise in temperature is accompanied by an increase in grain diameter and a consequent decrease in the porosity during densification[8].Consequently, microwave sintering can enhance the densification and improve uniformity of NTC thermistors.

3.1.1 Brief introduction of NTC thermistors

Negative temperature coefficient (NTC) thermistors are thermally sensitive resistors whose resistance decreases with increasing temperature. Their resistivity can be expressed by the following Arrhenius equation[9]: $\rho=\rho_0 \exp(B/T)$, where ρ_0 is the resistivity of the material at infinite temperature, T is the absolute temperature and B is the B constant, which is sometimes called the coefficient of temperature sensitivity. In fact, B constant indicates a sensitivity to temperature excursions and is given by $B=q/k$, where q is the activation energy for electrical conduction, and k is the Boltzmann constant[10]. They are widely used in various industrial and domestic applications, e.g., elements for the suppression of in-rush current, for temperature measurements and controls, and for compensation for other circuit elements[11].

3.1.2 Microwave sintering of NTC thermistor ceramics

Jin et al.[12, 13] successfully calcined and sintered $Mn_{0.43}Ni_{0.9}CuFe_{0.67}O_4$ samples by microwaves. Fig.1 compares the XRD patterns of powders calcined by microwave treatment and conventional heating, respectively. As can be seen, phase analysis of conventionally calcined $Mn_{0.43}Ni_{0.9}CuFe_{0.67}O_4$ powders shows metallic oxide as the main crystalline phase and a very minor amount of spinel phase. These results indicate that oxides were still not fully reacted. However, for the microwave heating, the complete spinel phase has obtained when powders were calcined at 650°C. Consequently, the Microwave sintering leads to a lower calcination temperature than conventional methods. In the conventional sintering processes, extremely high sintering temperatures and long holding times (several hours) under air atmosphere are applied in the fabrication of thermistor products to achieve the highest density and minimum porosity. Fig.2 shows the SEM micrographs from the fracture surface of sintered samples. Although the same sintering temperature and holding time (1000°C, 40 min) were applied, the microstructures of conventional and the microwave sintered samples were different. It can be seen from the Fig.2(a) and 2(b) that the microwave-sintered samples for both nearsurface and interior regions are practically identical, showing intergranular fracture and uniform grain size. Additionally, most pores are located at the isolated grain boundaries. In contrast, as shown in Fig.2(c) and 2(d), the conventionally sintered samples show exaggerated grain growth and many isolated and closed pores. The exaggerated grain growth may indicate a very high mobility of grain boundaries[14]. The variation in densification parameter of the sintered samples as a function of holding time at 1000°C is shown in Fig.3. It can be observed that the green compacts are well densified when sintered at 1000°C for 40 min, showing a densification of above 0.82 and porosity of below 4.5%. Microwave-sintered samples exhibit enhanced densification for the same holding time compared with the conventionally sintered samples. That is because the densification is a thermally activated process and the activation energy for microwave densification is lower than the value for conventional sintering[15, 16]. Fig.4 compares the B constant and resistivity (ρ) of twenty components by microwave and conventional sintering. Microwave sintering can obtain the components with well uniformity of B value and resistivity, of which the B_{avg} is 1930K (deviation of 1.47%) and resistivity ρ_{avg} is 135Ωcm (deviation of 4.45%). However, the B_{avg} is 1720K (deviation of 1.47%) and resistivity ρ_{avg} is 78Ωcm (deviation of 25.34%) for the conventionally sintered components. Therefore, microwave sintering is more effective in promoting uniformity and consistency of components compared to conventional sintering.

There is an increasing need for thermistors with high-precision and exchange-type in various industrial and domestic applications, such as temperature measurements and controls. In order to obtain NTC thermistor with low B value (2100 K), high-precision, exchange-type and fine homogeneity, $Mn_{0.43}Ni_{0.90}CuFe_{0.67}O_4$ NTC thermistor material precursors were prepared by the polymerized complex method using microwave sintering and conventional sintering[17]. The obtained results indicated that the particles microwave calcined at 650°C were small and uniform. The ceramics mainly consisted of rich-Cu phase and poor-Cu phase. The homogeneity of components is significantly increased by microwave sintering. Moreover, the rate of finished products is increased to 85% from 30% compared with the one of conventional sintering. The sintering activity and electrical properties of CoMnNiO based ceramic were investigated by Zhang et al.[18]. CoMnNiO NTC thermistor materials prepared by coprecipitation were sintered by microwave and conventional sintering. Compared with the conventional sintering, the samples prepared by microwave sintering have homogeneous density microstructure and fine grain size. The resistance deviation of components is 5% and 3% for conventional and microwave sintering, respectively. Electrical properties indicate that microwave sintering improves uniformity and consistency of components. In conclusion to this, microwave sintering method has potential superiority on synthesis NTC ceramic materials.

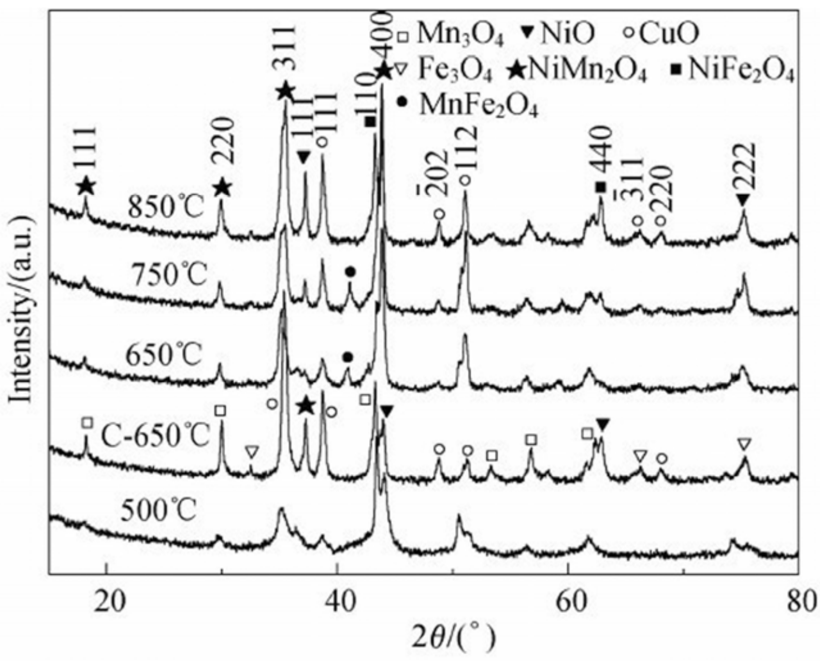


Fig. 1. XRD patterns of $Mn_{0.43}Ni_{0.9}CuFe_{0.67}O_4$ powder calcined at different temperature 500-850°C: microwave sintering with dwelling time of 30min; C-650°C: conventionally calcined at 650°C[12].

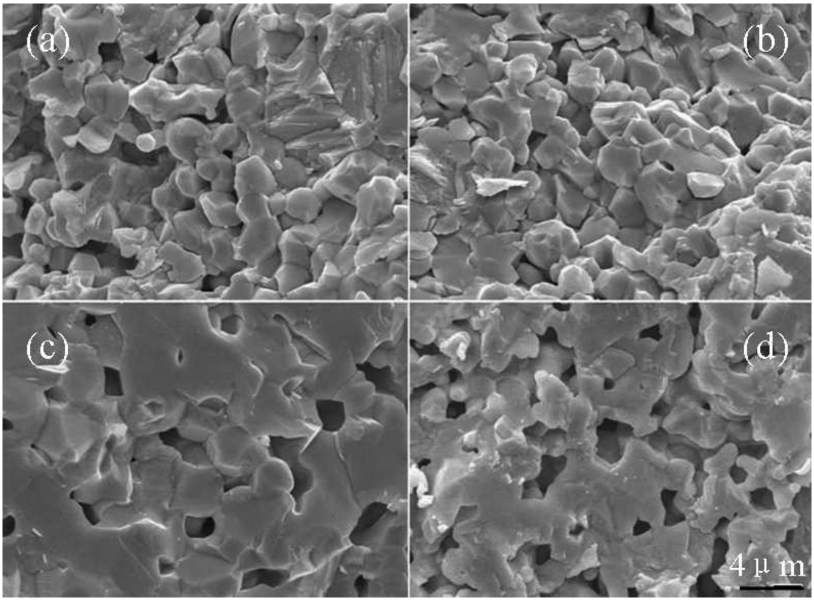


Fig. 2. SEM images of the fractures of samples: (a) near-surface region, microwave; (b) interior region, microwave;(c) near-surface region, conventional; (d) interior region, conventional[13].

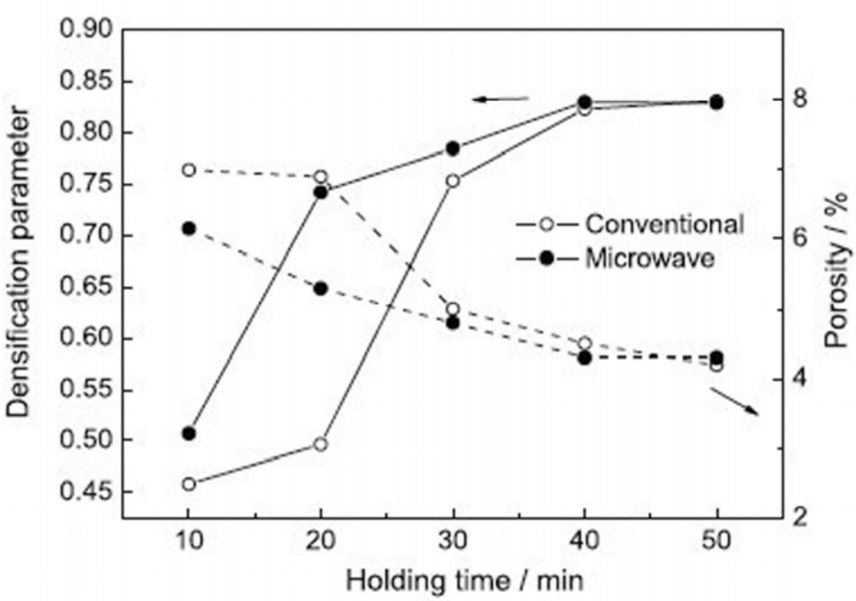


Fig. 3. The densification parameter and porosity of samples sintered for various holding time[13].

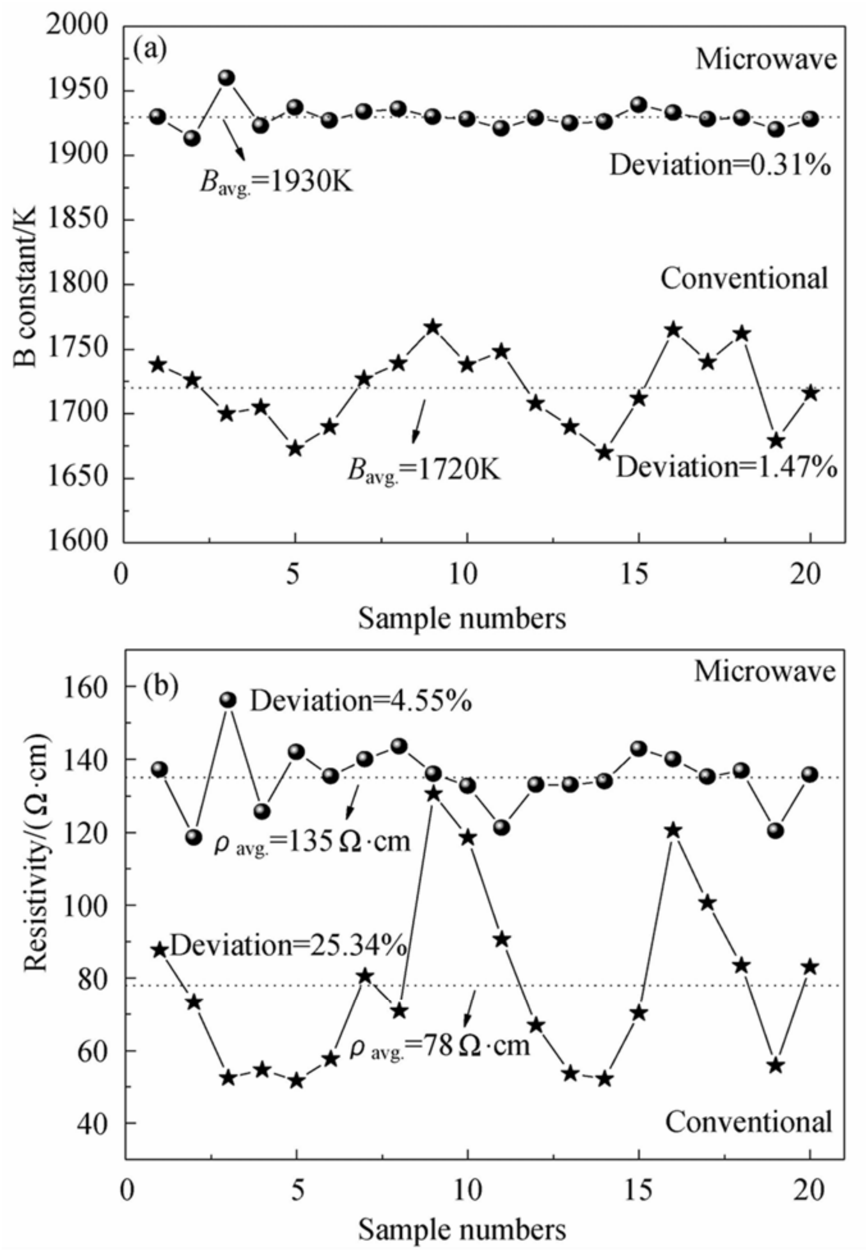
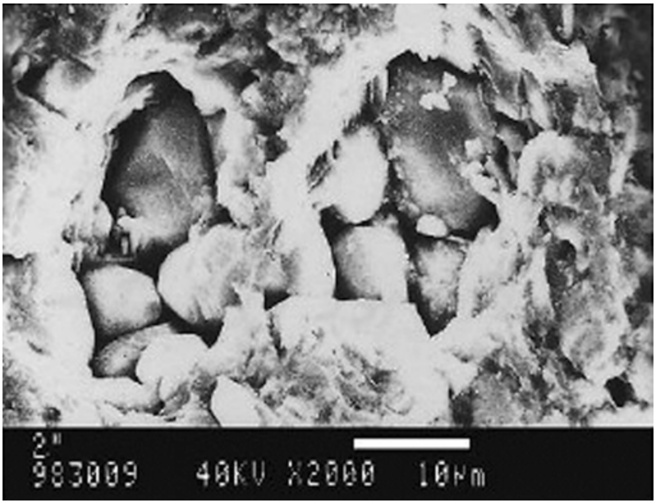


Fig. 4. Distribution of (a) *B* constant, (b) *ρ* for twenty components[12].

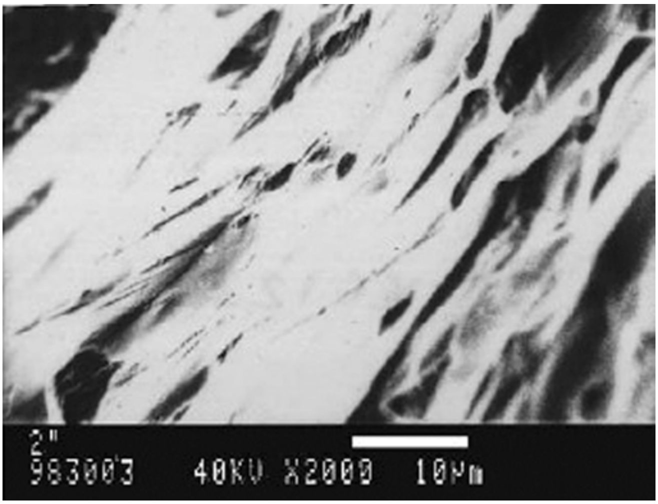
3.2 Microwave sintering of PTC thermistor ceramics

Positive temperature coefficient (PTC) thermistors are characterised by an increase in the electrical resistance with temperature. They are widely used in various industrial and domestic applications, such as electronic and electrical temperature control.

Chang et al. have studied the orientational growth of grains in doped $BaTiO_3$ PTCR materials by microwave sintering[19]. Fig.5 exhibits typical microstructures of sintered



(a)



(b)

Fig. 5. The microstructure of the samples: (A) conventional sintering; (B) microwave sintering[19].

sample. The conventional-sintered sample shows ecliptic spherical shape, whereas the microwave-sintered sample shows an orientational strip-like microstructure. The growth of grains in microwave-sintered BTO is obvious orientational, which is very different from the familiar conventional-sintered BTO. The XRD (Fig.6) analysis indicates that the perovskite structure of microwave-sintered BTO is tetragonal, whereas the conventional-sintered sample is cubic. The reason for this abnormal phenomenon can perhaps be attributed to the polarisation of BTO as a typical piezoelectric material in the microwave field, and also to the enhancement of grain diffusion by the microwave-sintered.

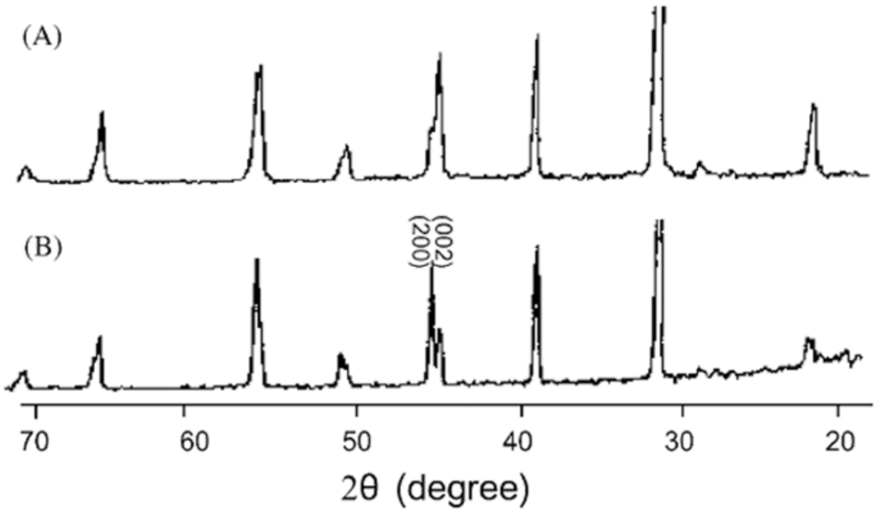


Fig. 6. XRD patterns of doped BTO samples: (A) conventional sintering; (B) microwave sintering[19].

3.3 The study of insulator materials for the microwave sintering of oxide thermistor ceramics

CoMnNiO series NTC and $BaTiO_3$-based PTC ceramics, having good dielectric coupling characteristic, can more easily couple with microwaves, therefore, generating heat to achieve sintering. However, due to the problems of thermal cracks during the microwave sintering and especially in the rapid cooling procedure, the production rate of oxide thermistor ceramics by microwave sintering is very low.

Chang et al. have successfully prepared $MgA1_2O_4$-$LaCrO_3$ insulator materials which mix $MgA1_2O_4$ spinel materials with superior thermal properties and $LaCrO_3$ perovskites materials with high efficiency absorption of microwave[20].The design of this kind insulating system solves the problems of thermal cracks often occur in the microwave sintering of many oxide ceramics, such as CoMnNiO series NTC ceramics and $BaTiO_3$-based PTC ceramics. Additionally, the $MgA1_2O_4$-$LaCrO_3$ insulator materials can produce a homogeneous heating for the samples in the microwave sintering, and grain crack-free and dense ceramic samples. Adopting $MgAl_2O_4$-$LaCrO_3$ susceptor in the temperature range of

1100-1200°C, microwave sintering of large-sized (50rum in diameter and 50mm in thickness) crack-free Co-Mn-Ni spinel oxide NTC ceramics has been achieved successfully[21]. Besides, $BaTiO_3$-based PTC ceramics (30mm in diameter) were microwave sintered at 950°C for 50min by the adoption of $MgAl_2O_4$-$LaCrO_3$ susceptor[20].

4. Summary

The fundamentals, applications of microwave sintering to thermistor ceramics and $MgA1_2O_4$-$LaCrO_3$ insulator materials for the microwave sintering of oxide thermistor ceramics are reviewed in this chapter. The advantages of microwave sintering against conventional sintering methods for thermistor ceramics are summarized as follows:(1) Microwave sintering consumes much lower energy than conventional sintering; (2) Higher heating rates can be attained and thus the sintering time reduces by using microwave sintering;(3) Generally higher density and better grain distribution can be achieved through microwave sintering. What's more, microwave sintering can enhance the densification rate and hence improve the uniformity and consistency of thermistors to a greater extent than the conventional sintering.

In the past year and half, significant developments and advances have taken place in the field of microwave sintering of ceramics. In spite of these successes, microwave processing has yet to see wide spread application in the ceramic industry. Additionally, more research must be conducted to have a full understanding of the process. It can be predicted that there is a great future for microwave sintering for the successful commercialization for specialty ceramics.

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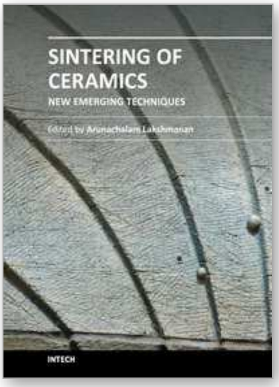

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The chapters covered in this book include emerging new techniques on sintering. Major experts in this field contributed to this book and presented their research. Topics covered in this publication include Spark plasma sintering, Magnetic Pulsed compaction, Low Temperature Co-fired Ceramic technology for the preparation of 3-dimesinal circuits, Microwave sintering of thermistor ceramics, Synthesis of Bio-compatible ceramics, Sintering of Rare Earth Doped Bismuth Titanate Ceramics prepared by Soft Combustion, nanostructured ceramics, alternative solid-state reaction routes yielding densified bulk ceramics and nanopowders, Sintering of intermetallic superconductors such as MgB2, impurity doping in luminescence phosphors synthesized using soft techniques, etc. Other advanced sintering techniques such as radiation thermal sintering for the manufacture of thin film solid oxide fuel cells are also described.