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Use of microwaves for the synthesis and processing of materials

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Abstract. An overview of the synthesis of materials under microwave irradiation has been presented based on the work performed recently. A variety of reactions such as direct combination, carbothermal reduction, carbidation and nitridation have been described. Examples of microwave preparation of glasses are also presented. Great advantages of fast, clean and reduced reaction temperature of microwave methods are emphasized. The example of ZrO_2-CeO_2 ceramics has been used to show the extraordinarily fast and effective sintering which occurs in microwave irradiation.

Keywords. Microwave synthesis; nitridation reaction; carbidation; glasses; microwave sintering.

1. Introduction

Synthesis and consolidation are two vital aspects of materials science particularly in respect of ceramics. One of the most important and attractive developments in this context is the use of microwaves for both synthesizing and sintering ceramics. The range of frequencies from 0·3 to 300 GHz in electromagnetic spectrum (wavelengths ranging from 1 m to 1 mm) constitute microwaves. Microwaves are coherent and polarized. Only two frequency windows of microwaves are available for industrial use and most microwave work reported to date is based on the use of 2·45 GHz sources. Microwave ovens which work at this frequency and at power levels of about a kW are in wide use (Osepchuk 1984).

It is generally believed that microwaves couple effectively with lossy materials and the primary action of microwaves occurs through very rapid heating. However, both physical and chemical characteristics seem to affect microwave coupling and hence microwave heating. This is amply illustrated in the literature particularly by microwave coupling of various forms of carbon. One important characteristic of microwave heating is that the entire volume of particles get heated up since generally the penetration depths are quite high. Thus the bulk heating and minimization of thermal gradients lead to modes of reaction as yet incompletely understood. Several materials couple effectively above a certain temperature probably because of the temperature dependent increase of dielectric loss. However, the phenomena enables immediate use of this aspect in microwave processing of pre-heated ceramic materials. The pre-heating itself could be accomplished by use of an inert second material which couples to microwaves at room temperature.

In this article, we first present the currently popular ideas about interaction of microwaves with matter. We then present examples of the preparation of several materials through different types of reactions assisted by use of microwaves. We also discuss consolidation of an important class of ZrO_2 ceramics which illustrates the powerfulness of the technique microwave sintering. The sections are subtitled accordingly.

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2. Microwave interaction with materials

The most notable effect of microwave irradiation is the heating effect. In microwave heating, unlike in conventional heating, heat is generated within the material itself instead of heat supplied from external sources. As a result of this internal and volumetric heating, thermal gradients and flow of heat during microwave processing are quite different from those observed in conventional heating. The schematic of conventional and microwave heating processes are shown in figure 1. The various advantages of microwave process over conventional heating have been discussed in great depth by Sutton (1989).

Microwaves obey the laws of optics—they are transmitted, reflected or absorbed depending on the nature of materials. Figure 2 describes briefly the action of microwaves in different types of materials. Generally insulators which have low dielectric loss are transparent and those with high dielectric loss absorb microwaves and get heated. Many insulators which are microwave transparent at room temperature absorb microwaves at higher temperatures. Also, inclusions of conductive and magnetic phases in transparent materials enhance microwave absorption.

Microwave coupling is related to complex permittivity of the material by the relation

$$\varepsilon'' = \varepsilon' - j\varepsilon'' = \varepsilon_0(\varepsilon_r' - j\varepsilon_{eff}''), \tag{1}$$

where $j = (-1)^{1/2}$, $\varepsilon_0 = 8{\cdot}86 \times 10^{-12}$ F/m, permittivity of free space, ε_r' is the relative dielectric constant and ε_{eff}'' is the effective dielectric loss factor.

When microwaves propagate through the material, an electric field is generated within the target material and it induces translational and rotational motions of the free and bound charges. They also excite the rotational modes of charge complexes such as dipoles. The resistance to the induced motions causes loss of microwave intensity in the material. The losses are frequency dependent and they attenuate the electric field which results in heating. The loss parameters are all combined into an effective relative dielectric loss factor, ε_{eff}''. The loss tangent is defined in term of ε_{eff}'' as

$$\tan\delta = \frac{\varepsilon_{eff}''}{\varepsilon_r'} = \frac{\sigma}{2\pi f \varepsilon_r' \varepsilon_0}, \tag{2}$$

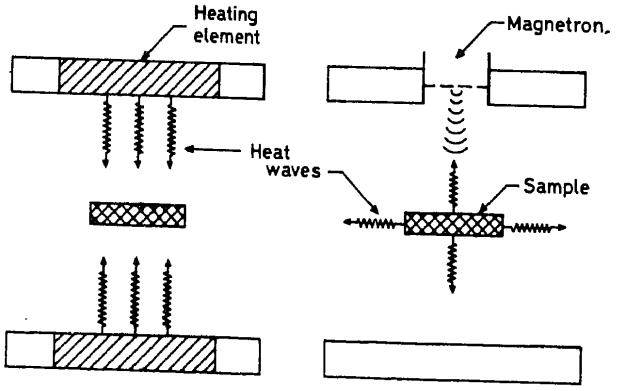

Figure 1. Representation of conventional and microwave heating patterns (schematic).

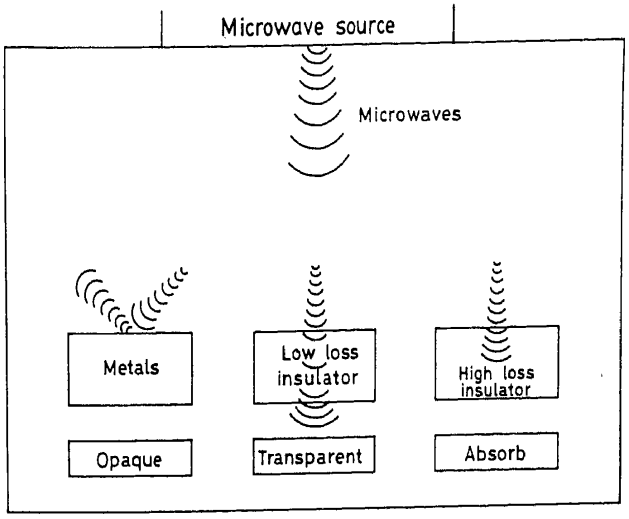

Figure 2. Behaviour of different types of materials in the microwave field (schematic).

where σ is the total effective conductivity (S/m) caused by conduction and displacement currents and f the frequency (GHz) of microwaves.

The power absorbed by unit volume, P is given by

$$P = 2\pi f \varepsilon_0 \varepsilon_r' \tan\delta E^2, \tag{3}$$

where $E(V/m)$ is the magnitude of the field. Therefore power absorbed varies linearly with the applied frequency, dielectric constant (ε_r) of the material and the effective loss factor ($\tan\delta$). It also varies with the square of internal electric field (E). The parameters f, ε_r', $\tan\delta$ and E are all also not entirely independent of each other. Electric field generated in the material further depends on its size, geometry, its location within the microwave cavity and the design on the cavity itself. Equation (3) indicates the nature of variables which determine the value of P.

A parameter D which denotes the depth of microwave penetration in the material at which the incident power is reduced by one half is given by the equation

$$D = \frac{3\lambda_0}{8{\cdot}686\pi \tan\delta(\varepsilon_r'/\varepsilon_0)^{1/2}}, \tag{4}$$

where λ_0 is the incident (or) free space wavelength. Thus D is higher for higher wavelengths or lower frequencies. But lower frequencies result in lower induced electric field (E) in the material which in turn causes less heating (see (3)). Thus there is an optimal range of useful microwave frequencies for material processing. The most commonly used microwave frequencies for materials processing are 0·915 GHz and 2·45 GHz. The loss factor of the material denoted by $\tan\delta$ varies with temperature. ε_r is also temperature dependent. Generally $\tan\delta$ increases slowly initially up to a temperature T_{crit} above which it increases steeply. Above T_{crit}, therefore $\tan\delta$ begins to rise and the material absorbs microwaves very efficiently which results in a rapid rise in the temperature. An exponential increase (runaway) in the temperature is noticed in materials and the phenomenon is referred to as thermal runaway. Thermal

runaway often causes undesirable hot spots in the material. By controlling the microwave power it is possible to prevent thermal runaway phenomenon in the material. Kenkre *et al* (1991) discussed thermal runaway phenomena in materials quantitatively.

The primary consequence of interaction of microwaves with materials appears to be rapid heating albeit with differences in details as compared to conventional heating.

3. Synthesis of materials

Microwave heating provides a uniquely advantageous method for the synthesis and sintering of materials. In the following we present synthesis of materials by different routes and induced by microwave irradiation.

3.1 *Direct combination*

3.1a *Chalcogenides:* Chalcogenides constitute a rich category of inorganic solids with many technological applications such as solar cells. The conventional solid state synthesis of chalcogenides is quite complex. Preparation of PbTe by conventional method involves cumbersome heating in rotary furnaces for several hours. In microwave assisted synthesis (Vaidhyanathan *et al* 1995a), it is accomplished very simply by mixing together stoichiometric quantities of metal and chalcogenide powders in sealed evacuated (5×10^{-5} torr) quartz tubes and subjecting them to microwave irradiation in a kitchen microwave oven operating at 2·45 GHz (maximum power 980 W)*. Fine metal powders absorb microwaves and eddy currents are generated in the particles which result in heating. Exposure times varied from 5–20 min for complete reaction. Given in figure 3 is the X-ray diffractogram (XRD) of chalcogenide products (PbSe, PbTe, ZnS, ZnSe and Ag_2S) obtained in this manner. Notable is the high phase purity of the products. The lattice parameters matched very well with the reported values.

3.1b *Metal vanadates*: Vanadates like $Bi_4V_2O_{11}$ and PbV_2O_6 exhibit interesting electrical properties like ferroelectricity and are therefore technologically important materials. Conventional methods for their preparation are very tedious. Metal vanadates (Vaidhyanathan *et al* 1995a) of bismuth ($Bi_4V_2O_{11}$) and lead (PbV_2O_6) have been prepared starting with reagent grade materials of V_2O_5, Bi_2O_3 and PbO. The reactions were carried out by placing stoichiometric mixtures of component oxides in a quartz crucible which was placed in a microwave oven and irradiated for 15 min. V_2O_5 absorb microwaves efficiently and the temperatures reach up to 1000 K. The products were allowed to anneal in the furnace for 2 h. The XRD patterns of metal vanadates prepared by microwave irradiation are shown in figure 4. The products exhibited high phase purity and the lattice parameters are as follows: $Bi_4V_2O_{11}$: a = 16·86 Å, b = 16·62 Å and c = 15·33 Å and PbV_2O_6: a = 9·799 Å, b = 3·670 Å and c = 12·712 Å. These are in very good agreement with literature reports (Varma *et al* 1990).

It was confirmed that annealed $Bi_4V_2O_{11}$ sample exhibits an endothermic $\alpha \rightarrow \beta$ transformation around 725 K as reported by Abraham *et al* (1988) by using

*All reactions described in this paper were conducted in this type of microwave oven.

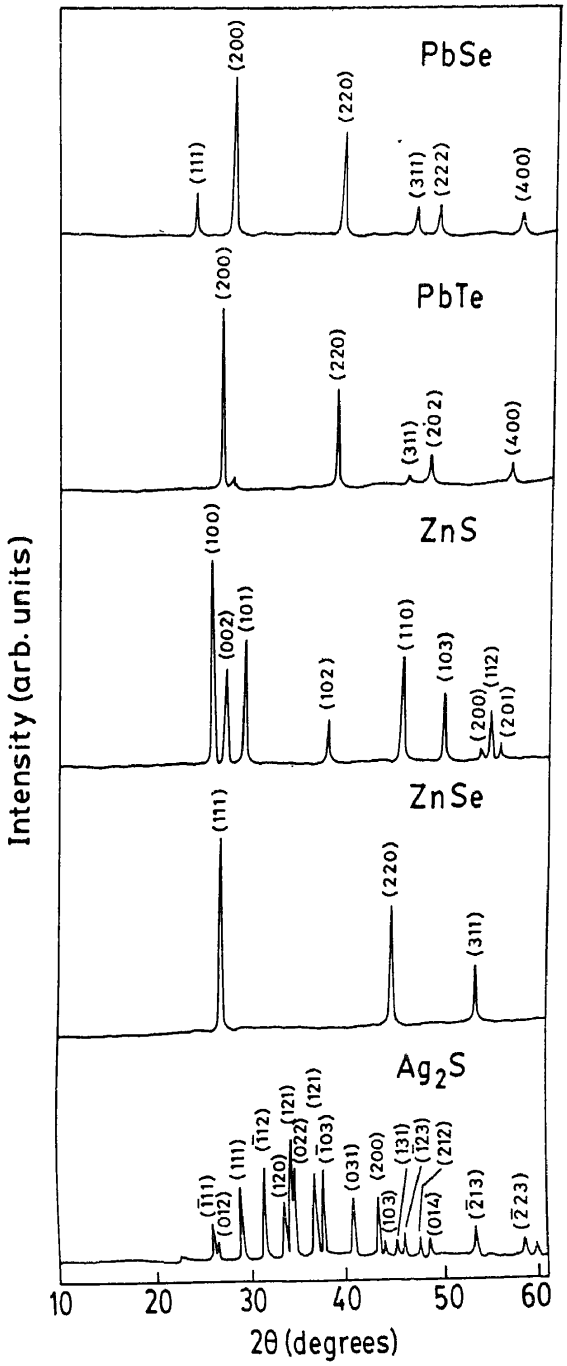

Figure 3. X-ray diffractograms of microwave prepared metal chalcogenides.

differential scanning calorimetry (DSC). The IR spectrum of PbV_2O_6 has a sharp band at 960 cm^{-1} and broad bands at 870, 830, 750, 700, 530, 470, 420 cm^{-1} all of which are in good agreement with the previous reports (Tsuzuki *et al* 1992).

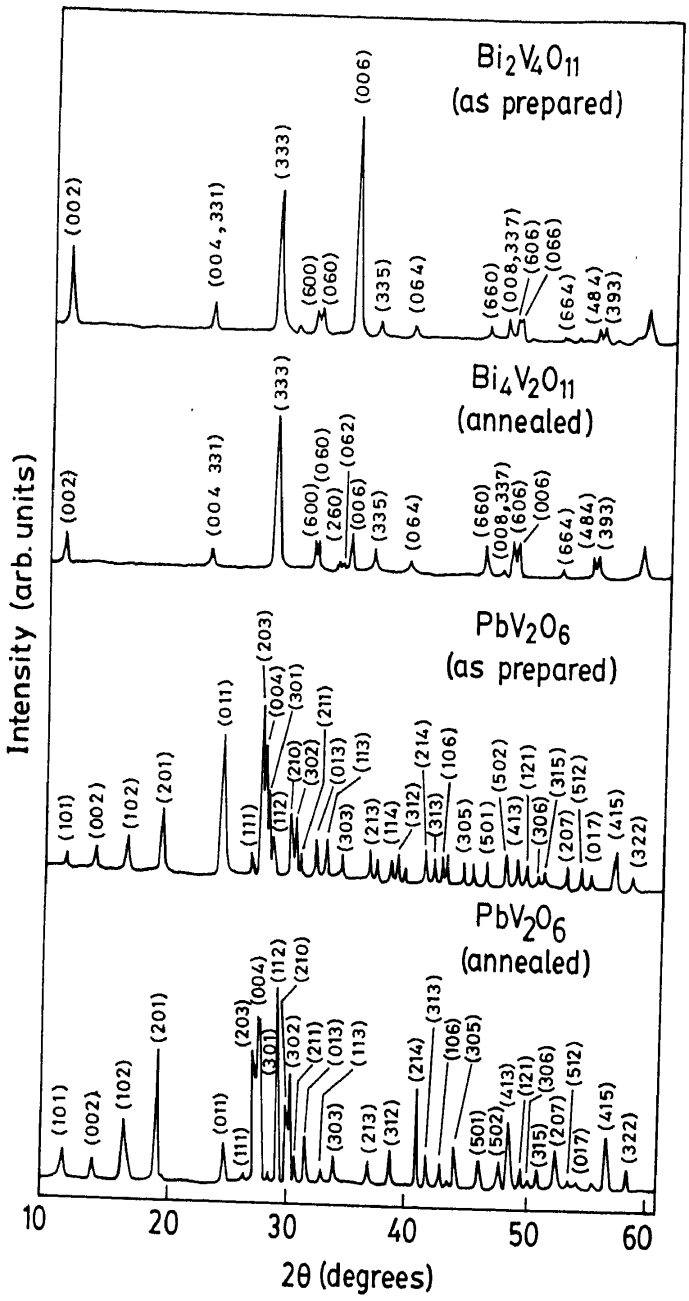

Figure 4. X-ray diffractograms of the metal vanadates prepared by microwave method.

4. Carbothermal reduction

4.1 *Deoxygenation of layer and chain containing oxides*

Some of the industrially important oxides like MoO_2 and Cr_2O_3 are generally obtained by reduction of corresponding higher valent oxides like MoO_3 and CrO_3. It

is found that carbothermal reduction under microwave irradiation is an amazingly fast and simple method for this purpose provided higher valent oxides have layered structure or consists of chains of oxide polyhedral units. Many layered oxides namely MoO_3, V_2O_5, α-$VOPO_4 \cdot 2H_2O$ and $Ag_6Mo_{10}O_{33}$ are reduced to MoO_2, VO_2, VPO_4 and $(Ag + MoO_2)$ respectively by graphitic carbon under microwave irradiation (Vaidhyanathan 1995b). Similarly CrO_3 which consists of chains of tetrahedrally coordinated chromium atoms is reduced to Cr_2O_3. The products were characterized using XRD, DSC, IR and ESR spectroscopies.

Experiments have been carried out using analar grade chemicals of MoO_3, V_2O_5 and CrO_3 (for preparation of MoO_2, VO_2 and Cr_2O_3) and high purity graphitic carbon. α-$VO_4PO_4 \cdot 2H_2O$ was prepared by the procedure described by Johnson *et al*

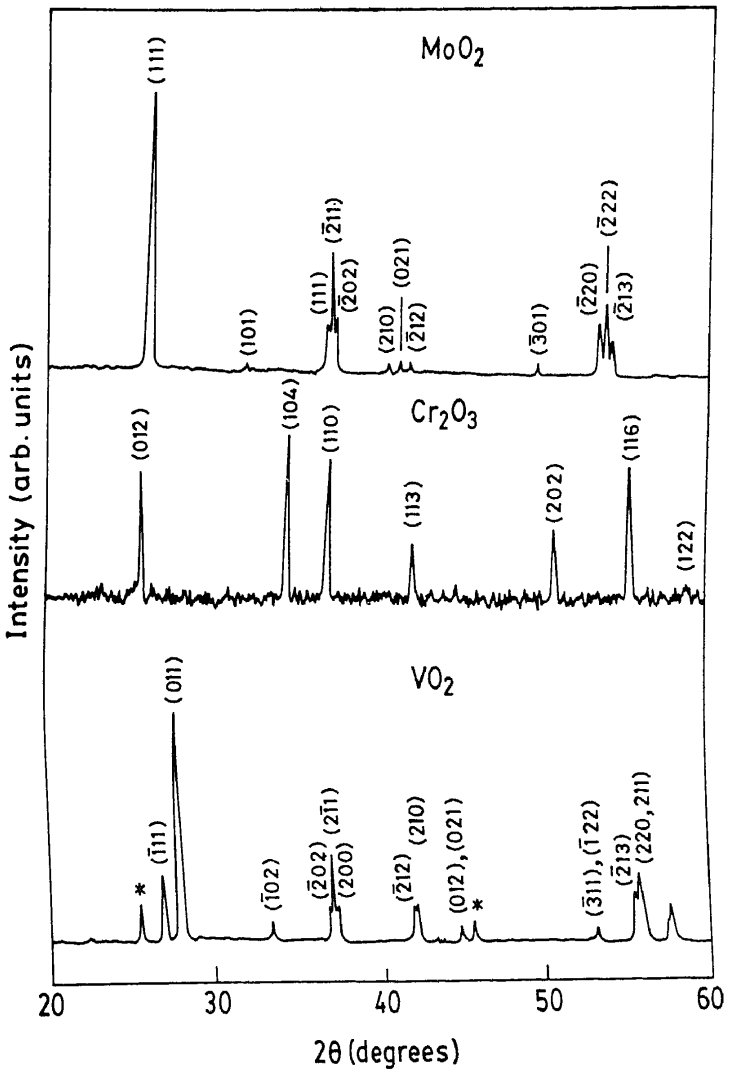

Figure 5. X-ray diffractograms of MoO_2, Cr_2O_3 and VO_2 (* indicates the peaks corresponding to the high temperature phase of VO_2).

(1982). $Ag_6Mo_{10}O_{33}$ was prepared by heating the mixture of Ag_2MoO_4 and MoO_3 in air (Rosner and Lagaly 1984). Initially the powders were thoroughly mixed with graphitic carbon in 3:1 weight ratio and exposed to microwaves in a silica crucible for 4 to 5 min. Remaining carbon can either be washed out or burnt in air. Experiments reveal (Vaidhyanathan *et al* 1995b) that these reactions occur entirely in the solid state.

XRD of the products formed are shown in figure 5. Lattice parameters of the microwave synthesized reduced compounds have been compared with the existing data and are given in table 1. The DSC trace of VO_2 exhibits a clear endothermic transition at 340 K which corresponds to semiconductor metal transition of VO_2. The room temperature electron spin resonance (ESR) signal of V^{4+} in α-$VOPO_4 \cdot 2H_2O$ shows anisotropic hyperfine structure which compares well with the reported spectrum (refer figure 6). The product VPO_4 exhibits a much simpler ESR spectrum due to a V^{3+} ion which compares well with the spectrum of V^{3+} of V_2O_3. Matching of ESR spectrum of microwave synthesized Cr_2O_3 and commercial Cr_2O_3 has provided additional confirmation.

It is interesting to note that though MoO_3 and WO_3 are chemically similar only layered MoO_3 undergoes reduction reaction. It is clear demonstration of how structural chemistry plays an important role in these reactions. Also the non-layered materials such as TiO_2, SnO_2, Nb_2O_5 and ZrO_2 are not reduced by carbon in similar microwave experiments.

It is likely that the unshared oxygen which is connected to Mo weakly through the longer Mo–O bond of distance 2·33 Å is reacted away by the graphitic (sp^2) carbon resulting in the reduction of MoO_3. A similar mechanism is suggested for V_2O_5 also. In dehydrated α-$VOPO_4$, the VO_5 square pyramids are connected by interlayer oxygen which can readily react with carbon which results in the formation of V^{3+} phosphate. Removal of oxygens from interlayer region in $Ag_6Mo_{10}O_{33}$ destabilizes the structure and it undergoes a complete decomposition to $Ag + MoO_2$. Presumably, Ag^+ is also reduced to Ag^0. Similar reduction appears to occur in CrO_3 which consists of $[CrO_{2/2}O_2]$ chains. Microwave route thus provides an elegant and

Table 1. Lattice parameters of the microwave prepared lower valent oxides.

Compound	Lattice parameters		Reference
	Calculated	Reported	
MoO_2	a = 5·615 Å	5·607 Å	(NBS Monograph 1981)
	b = 4·859 Å	4·860 Å	
	c = 5·533 Å	5·537 Å	
	β = 119°35′	β = 119°35′	
Cr_2O_3	a = 4·962 Å	4·959 Å	(McMurdie 1987)
	c = 13·582 Å	13·594 Å	
VO_2	a = 5·742 Å	5·743 Å	(Anderson 1954)
	b = 4·519 Å	4·517 Å	
	c = 5·377 Å	5·375 Å	
	β = 112°56′	β = 122°60′	
VPO_4	a = 5·220 Å	5·245 Å	(Tudo and Carton 1979)
	b = 7·770 Å	7·795 Å	
	c = 6·266 Å	6·285 Å	

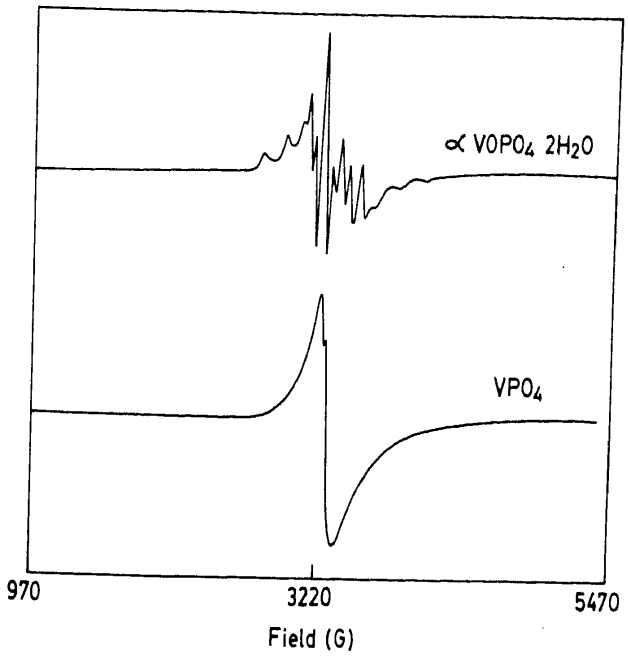

Figure 6. Room temperature ESR spectra of α-$VOPO_4 \cdot 2H_2O$ (reactant) and VPO_4 (product).

structure selective method of reduction in solid state. Further the method is very fast (5 min) compared to long (such as 90–100 h for the preparation of MoO_2) and tedious conventional methods.

5. Carbidation reaction

Silicon carbide (SiC) is one of the most important ceramics used in several applications. It can be prepared by irradiating a well prepared mixture of pure silicon and charcoal powders with 2·45 GHz microwaves. In our experiments the mixture was taken in a quartz container and exposed to microwaves up to a maximum of 10 min. Reaction was carried out in both air and iodine as ambients. The details of these have been discussed by Ramesh *et al* (1994). All the samples were identified by XRD. The reaction in air (particularly with excess carbon) leads to formation of silica up to about 15% which could be removed by chemical leaching. But silicon–carbon reaction carried out in iodine atmosphere gave only β-SiC of good phase purity (refer figure 7). Iodine atmosphere was created by carrying out a reaction between KI and V_2O_5 in a separate crucible along side (Si + C) mixture.

Maximum temperature attained by silicon–carbon mixture at 980 W power is 1173 K. This temperature is far less than the temperature (1673 K) required for initiation of silicon–carbon reaction in conventional process. Microwave heating carried out separately revealed that silicon is a poor microwave absorber whereas carbon is a good absorber.

It has been suggested (Ramesh *et al* 1994) that the rapidity of the reaction is likely to be a consequence of the effective use of reaction enthalpy of $Si + C \rightarrow SiC$ throughout

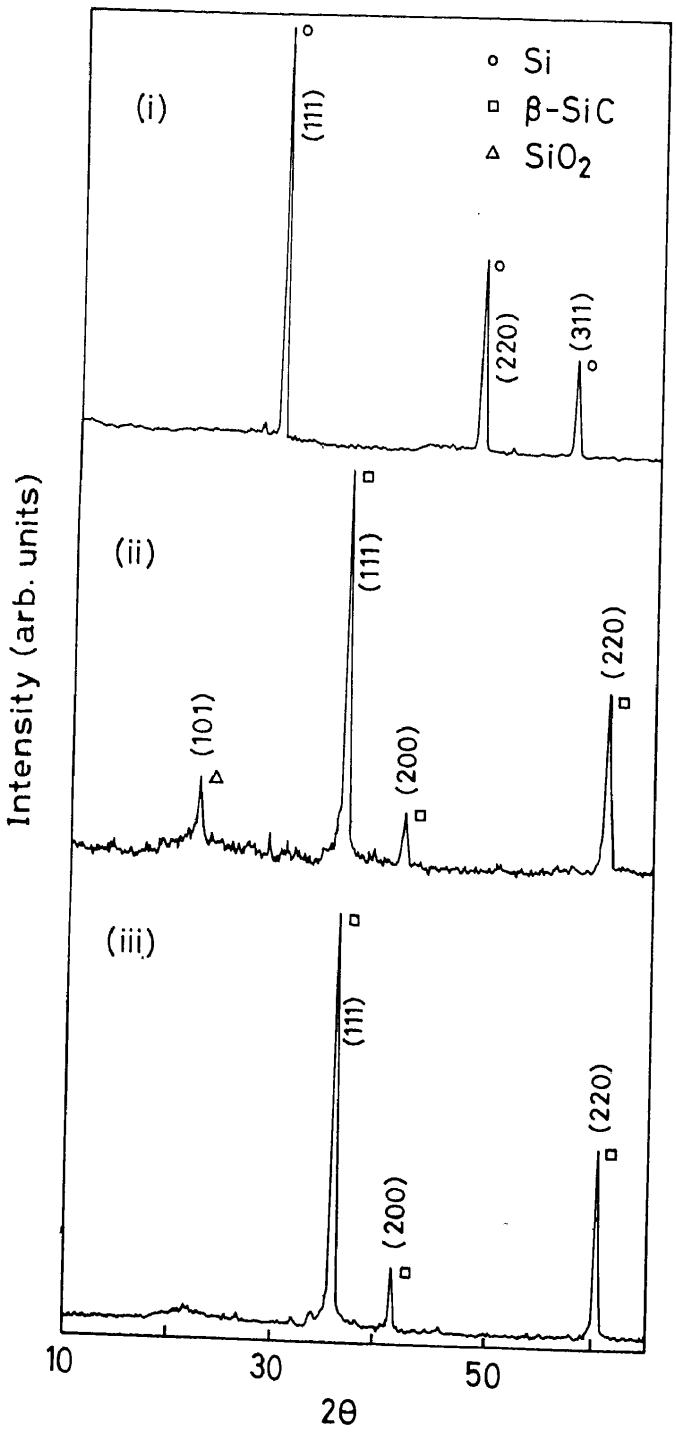

Figure 7. X-ray diffractogram of (i) silicon-carbon initial reactant mixture, (ii) reaction products formed in air after 10 min and (iii) reaction product formed in iodine atmosphere after 10 min.

the reaction mixture. The local heating of the reactants which absorb microwaves more efficiently escalates the rate of reaction. The lower (1000 K) temperature of the reaction itself could be due to the possible microwave excitation of graphitic bonds during silicon–carbon reaction.

The microwave assisted preparation of SiC is notable for three aspects: (i) very short time scale of the reaction, (ii) lower reaction temperatures and (iii) very high phase purity of the product.

6. Nitridation reaction

It is found that microwave irradiation assists nitridation reaction as well. Aluminium nitride is an important and high-cost ceramic required in the electronic industry (Sheppard 1990). Besides, being an insulator, it possesses very attractive properties such as high thermal conductivity, low thermal expansivity and low dielectric constant. The method available for AlN synthesis involves high temperatures and handling atomized Al powder (Weimer *et al* 1994). Preparation by carbothermal reduction and nitridation (Cho and Charles 1991) starting with Al_2O_3 is also both cumbersome and time consuming. We have found (Ramesh and Rao 1995) that the synthesis of aluminium nitride can be achieved by the use of microwave irradiation of a mixture of aluminium and carbon powders in pure nitrogen. The details of the experiment and the possible reaction mechanisms are discussed by Ramesh and Rao (1995). The reaction between aluminium and nitrogen is highly exothermic. The temperature of reaction varies between 1373 K and 1573 K. The reaction does not proceed to completion in one step since AlN layers are formed on the surface of aluminium particles, which prevents further nitridation. However, nitridation of aluminium powder occurs at surprisingly low temperatures (1200 K) and at exceedingly fast rates. The microwave irradiation was interrupted every 15 min and the powder was ground so that the surface covering with AlN was broken down. The effect of grinding on the product formation is shown in figure 8. In the first 15 min nearly 40% of the products was formed. But without grinding the converted amount remained essentially unaltered even after 90 min. But with intermittant grinding nearly full conversion was achieved in about 120 min.

The resulting AlN powders were characterized using XRD, TEM, IR and particle size analysis.

The nitridation reaction was highly oxygen sensitive. Only when high pure nitrogen (99·995%) gas was used formation of pure AlN was observed. But even when 99·5% pure gas was used considerable amount of Al_2O_3 was found to form. AlN powders failed to reveal any XRD detectable oxide phase after burning out excess carbon at 973 K.

Infrared spectra of the microwave synthesized sample compared very well with the spectra of commercial AlN sample (see figure 9). Both give a strong and broad absorption band in the range of 1100–350 cm^{-1} with a maximum at 682 cm^{-1}. This corresponds to –Al–N– stretching vibration frequency in the wurtzite structure.

Some important features in microwave assisted synthesis are (i) the temperature does not rise beyond 1200 K; the silicaware remains unaffected, the charge becomes only red hot and no thermal runaway is observed, (ii) the aluminium particles, whose average size is 15 μm, does not appear to melt or agglomerate and (iii) the complete conversion of Al to AlN (including interruption times) is under 2h.

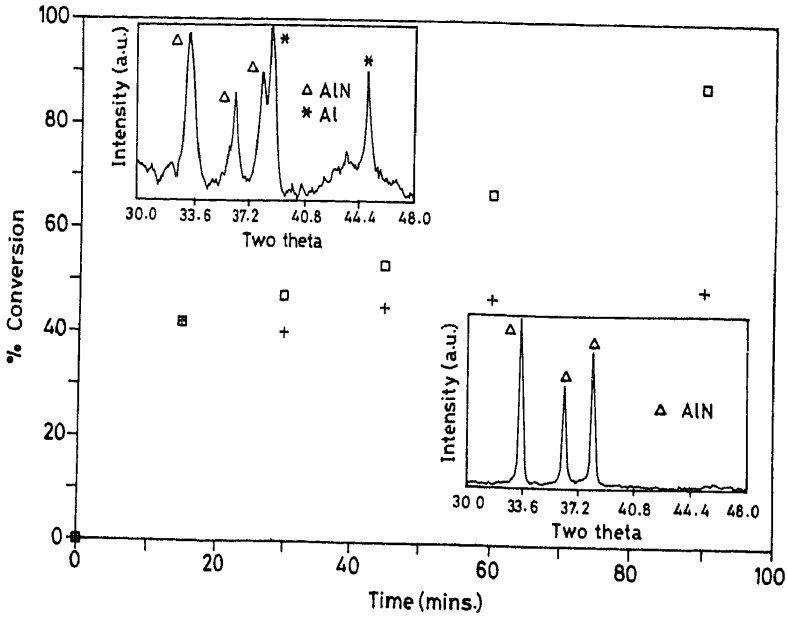

Figure 8. Amount of AlN formation against microwave exposure time; □, with intermediate grinding; +, without intermediate grinding. Top inset: X-ray diffractogram of the product mixture after 15 min of microwave exposure (no grinding). Bottom inset: X-ray diffractogram of the product mixture after 120 min of microwave exposure (ground eight times).

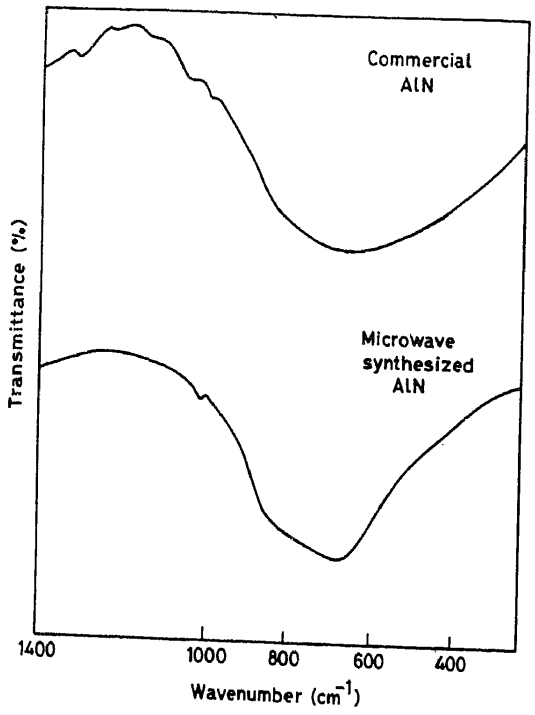

Figure 9. Infrared spectra of commercial AlN and AlN synthesized using microwaves.

It has been suggested that microwave coupling may be due to eddy current generation in aluminium particles and due to the high microwave susceptibility of carbon. However, the reaction appears to be directly microwave activated at the aluminium surface in an unclear manner and is not associated with the melting of aluminium particles. The product AlN is not a microwave absorber and hence apparently no further heating occurs. The process involves intermediate grinding and ensures formation of very fine (nanosized) AlN powder.

7. Preparation of glasses

Glasses are very easily prepared by melting mixture of the ingredients if at least one of the ingredients is a microwave susceptor (Vaidhyanathan *et al* 1994). The melts are quenched between polished stainless steel plates. Various glasses prepared by this technique is given in table 2. The T_g's of glasses determined using DSC are in good agreement with literature values (table 2). We have observed that oxides such as V_2O_5, WO_3, CuO, ZnO and SiO_2 gel and halides like AgI and CuI efficiently couple with microwaves and temperatures of up to ≈ 1000 K are easily attained. Homogeneity in heating is achieved by fine mixing of the initial powders. The process is extremely fast. Undesirable aspects such as loss of materials and oxidation by ambient air etc are easily avoided.

In the preparation of CuI containing glasses by conventional procedure, copper is known to oxidize to the extent of 12–15%. But when melted by using microwaves the maximum extent of Cu^{2+} was found to be only 0·9%. In another procedure in which the melting was performed in NH_3 atmosphere the oxidation of copper to Cu^{2+} was further reduced to 0·69% (ammonia atmosphere was created by heating a mixture of ammonium metavanadate and V_2O_5 in another crucible kept in the microwave oven). Cu^{2+} was estimated using ESR.

But the most important observation in this procedure is that the temperatures level off once the mixtures are melted and at different values for different mixtures. Since melting alters the chemistry of the mixtures and also its physical state the microwave absorption characteristics change. This feature acts as an autocontrol and the temperature of glass forming melts level off even when the microwave power is on.

8. Sintering of ZrO_2–CeO_2 ceramics

As noted earlier, one important advantage of microwave irradiation is the rapid heating rate. This leads to short processing durations and low power requirements as compared to conventional heating. It is therefore obvious that microwaves can be employed for sintering applications. Reports (Sutton 1989) exist on microwave sintering of many ceramic materials. We discuss here a method of sintering ceramics which are not good microwave susceptors at ordinary temperatures. The method can be of quite general utility.

ZrO_2–CeO_2 ceramics are known for their excellent mechanical properties. It is known that CeO_2 toughened ZrO_2 ceramics are potential electrode materials due to their mixed conduction. In conventional sintering process temperatures greater than 1873 K are required to achieve good sintering densities. Although ZrO_2 and CeO_2 are not good microwave absorbers at room temperature they exhibit good microwave

Table 2. List of glasses formed using microwave heating.

No.	Glass system	T_g(K)	Preparation conditions: Time (min)	Crucible used	Type of quenching	Reference
1	$xPbO:(100-x)V_2O_5$ [x = 40–50]	520–522	5	S	SSPQ	(Denton *et al* 1954; Tsuzuki *et al* 1992)
2	$50GeO_2:50V_2O_5$	491	6	S	SSPQ	(Denton *et al* 1954)
3	$33BaO:67V_2O_5$	551	5	S	SSPQ	(Denton *et al* 1954)
4	$30Na_2O:30B_2O_3:40V_2O_5$	470(468)	6	S	SSPQ	(Muthupari *et al* 1994)
5	$50AgI:25Ag_2O:25MoO_3$	348(340)	5	S	QPQ	(Shastry and Rao 1989)
6	$50AgI:25Ag_2O:25WO_3$	419(427)	6	S	QPQ	(Shastry and Rao 1989)
7	$50AgI:25Ag_2O:25CrO_3$	298(294)	3	S	QPQ	(Shastry and Rao 1989)
8	$50AgI:33Ag_2O:17GeO_2$	392(402)	5	S	QPQ	(Minami *et al* 1980)
9	$60AgI:20Ag_2O:10MoO_3:10WO_3$	345	3	S	QPQ	(Prasad and Radhakrishna 1988)
10	$40AgI:30Ag_2O:15WO_3:15B_2O_3$	460	5	S	QPQ	(Sidhu *et al* 1991)
11	$60AgI:20Ag_2O:10MoO_3:10V_2O_5$	351	2	S	QPQ	(Sathyanarayana and Radhakrishna 1988)
12	$30CuI:35Cu_2O:35MoO_3$					
	(in air)	390	3	S	SSPQ	
	(in NH_3 atm.)	393(404)	10	S	SSPQ	(Machida *et al* 1988)
13	$xB_2O_3:(45-x)PbO:55V_2O_5$ [x = 0–20]	520–515	7	S	SSPQ	(El-Sharkawy *et al* 1988)
14	$xSiO_2:(45-x)PbO:55V_2O_5$ [x = 0–15]	520–531	5	PZ	SSPQ	
15	$xZnO:(45-x)PbO:55V_2O_5$ [x = 0–40]	520–541	5	S	SSPQ	
16	$xMoO_3:(45-x)PbO:55V_2O_5$ [x = 0–35]	520–515	5	S	SSPQ	
17	$xCuO:(45-x)PbO:55V_2O_5$ [x = 0–20]	520–536	5	S	SSPQ	
18	$xWO_3:(45-x)PbO:55V_2O_5$ [x = 0–15]	520–531	5	S	SSPQ	
19	$xBi_2O_3:(45-x)PbO:55V_2O_5$ [x = 0–10]	520–537	4	S	SSPQ	

SSPQ, Stainless steel plate quenching; QPQ, quartz plate quenching; S, silica crucible; PZ, porous zirconia crucible.

susceptibility at high temperatures (> 773 K). Thus a secondary microwave absorber which does not react with either ZrO_2 or CeO_2 can be used to raise the temperature initially to ≈ 800 K above which ZrO_2 and CeO_2 themselves couple to microwave field. Such a secondary absorption is provided by β-SiC which is itself readily prepared by microwave methods (see earlier section).

Detailed experimental procedure is given elsewhere (Ramesh *et al* 1995). Commercial ZrO_2 and CeO_2 powders were used as starting materials. The pellets were made using the powder mixtures of ZrO_2 and CeO_2 of various compositions over the entire composition range. Green densities were measured. These pellets were placed inside β-SiC powder which was kept in a quartz crucible and irradiated with microwaves of 2·45 GHz frequency. Generally, the duration of sintering was 35 min. Sintered samples were characterized using XRD, SEM and density measurements. Microhardness and fracture toughness values were also measured using variable loads.

Entire range of compositions between ZrO_2 and CeO_2 were found to be readily sintered (figure 10). In most of the cases, sintering densities were well above 95%. It was observed that the sintering densities vary linearly with mole fraction of CeO_2. Thus although direct sintering of ZrO_2 and CeO_2 is not possible as their microwave

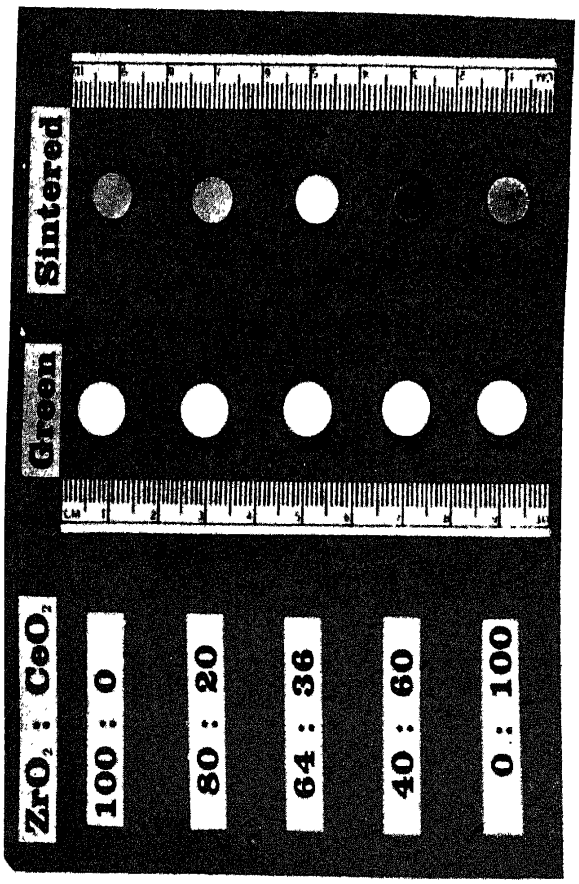

Figure 10. Photograph of ZrO_2–CeO_2 pellets (both green and sintered) with different compositions.

absorption is poor at room temperatures, microwave heating of β-SiC in which they are immersed preheats the pellets which absorb microwaves at elevated temperatures. A similar trend was observed with CeO_2. The temperatures of the pellets have been found to shoot up to 1773 K.

The phase field of sintered products were found to be similar to those observed in conventional sintering. Peak intensities of the ($\bar{1}11$) peak of monoclinic, (101) of tetragonal, and (111) of cubic phases were considered for phase content calculations. The variation of phase contents with ceria percentage is shown in figure 11. Even at 4% CeO_2 tetragonal phase (T_{ss}) is found to be present along with monoclinic (M_{ss}) phase. Above 20% only tetragonal phase (T_{ss}) is present. T_{ss} phase extends up to 44% CeO_2 above which both cubic and tetragonal phases appeared till 76% CeO_2. Above this percentage of ceria only cubic solid solutions were found to form. The lattice parameters were calculated using PROSZKI software and is given in table 3. ϕ-phase ($Ce_2Zr_3O_{10}$) formation was not observed in any of the compositions which confirms the observations of Tani *et al* (1983).

We have also noted that phase formation in certain compositions depends strongly on the sintering duration. In the $M_{ss} \rightarrow T_{ss}$ phase field with 12% CeO_2, sintering for 35 min results in 60% monoclinic and 40% tetragonal phases. The proportion of tetragonal phase increases with sintering time and about 95% tetragonal phase has formed after sintering for 105 min. Scanning electron micrograph of the etched top surface of this pellet is shown in figure 12. Thus phase boundaries in figure 11 obtained using 35 min should be treated as only approximate.

The hardness values are low for monoclinic phase whereas the Vickers hardness number (VHN) value increases and attains a maximum in the mixed tetragonal and cubic phase region. A maximum value of ≈ 1200 is reached in this region. For pure cubic phase the hardness values were again low. The scanning electron micrographs indicate the presence of microphases in the sintered samples. Hence fracture toughnesses, K_{IC}, are in fact microstructure dependent and only an apparent fracture

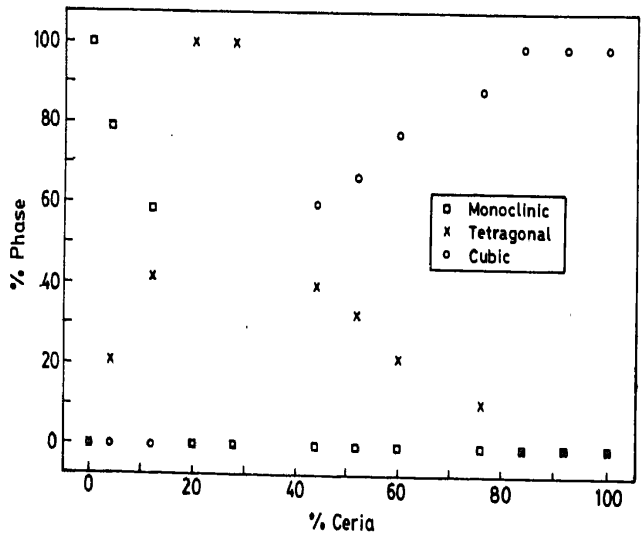

Figure 11. Variation of phase contents with ceria percentage.

Table 3. Sintering of ZrO_2–CeO_2 pellets by use of microwave irradiation.

Sample code	Composition ZrO_2:CeO_2	Time of sintering (min)	Volume change (%)	Green density (g/cc)	Sintered density (g/cc)	Relative density (%)
A0	100:0	35	32·4	3·53	5·66	95
A1	96:4	35	29·2	3·55	5·33	90
A2	88:12	35	30·2	3·69	5·93	95
A3	80:20	35	34·4	3·67	6·08	99
A4	72:28	35	27·6	3·74	6·16	98
A5	64:36	35	32·0	3·80	5·96	94
A6	56:44	35	35·0	3·82	5·87	91
A7	48:52	35	33·6	3·94	6·29	96
A8	40:60	35	31·3	4·00	6·39	96
A9	32:68	35	31·4	4·26	6·49	96
A10	24:76	35	30·4	4·35	6·77	99
A11	16:84	35	28·8	4·25	6·41	92
A12	8:92	35	32·7	4·28	7·01	99
A13	0:100	35	27·8	4·39	6·69	93
G0	100:0	35	35·3	3·44	5·63	95
G1	97:3	35	30·2	3·59	5·70	95
G2	94:6	35	32·9	3·60	5·70	95
G3	91:9	35	30·8	3·59	5·85	97
G4	88:12	35	27·0	3·57	5·84	96
G5	85:15	35	27·0	3·72	5·72	94
Ce(3)	95:5	35	34·1	3·58	5·60	94

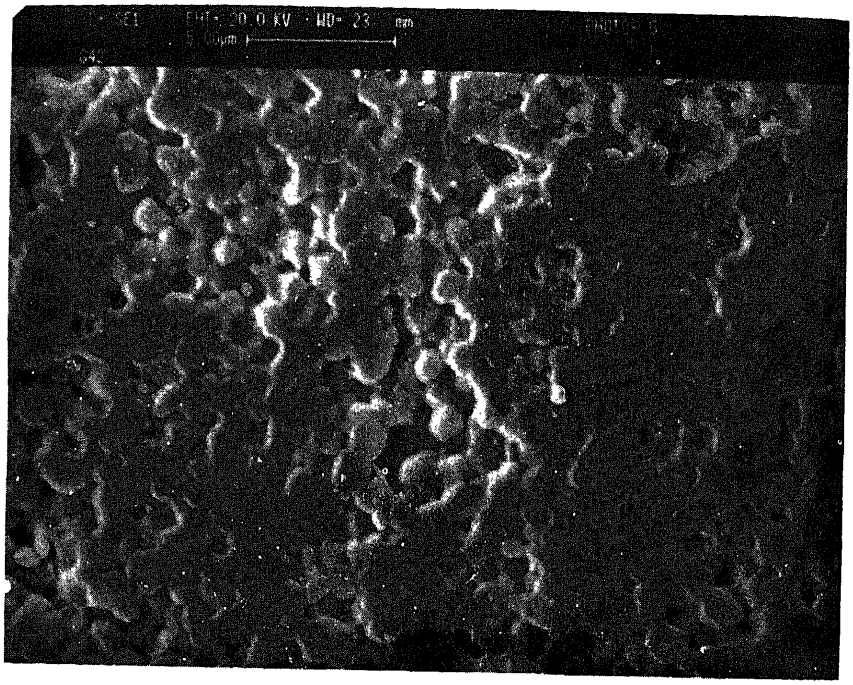

Figure 12. Scanning electron micrograph of the top surface of an etched pellet with 88 ZrO_2:12 CeO_2 composition.

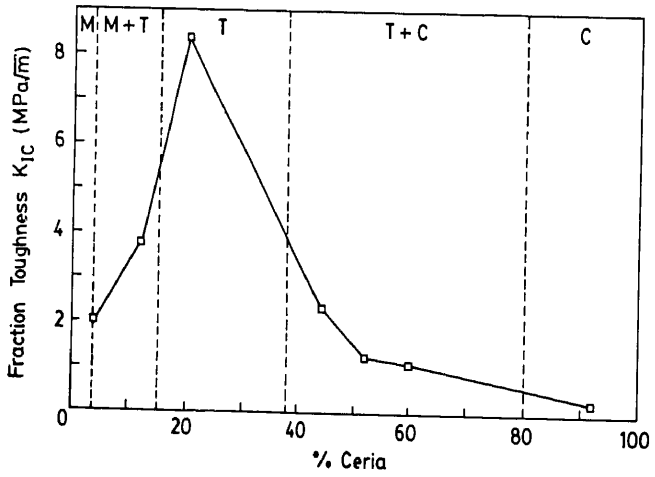

Figure 13. Variation of apparent fracture toughness values with ceria percentage.

toughness value of K_{IC} is assigned. Apparent fracture toughness value is maximum for the tetragonal phase particularly around 20% CeO_2 content (figure 13). The rather high apparent fracture toughness value of 8 MPa$\sqrt{m}$ could be due to the attendant $M_{ss} \rightarrow T_{ss}$ phase transition. K_{IC} is severely reduced when tetragonal phases are partly substituted by either cubic or monoclinic phase.

We conclude that microwave irradiation provides the fastest means of sintering ZrO_2–CeO_2 ceramics. Theoretical densities well over 95% are achieved in very short durations (35 min) by this method. Micrographs indicate that interparticle sintering could have preceded by thermal shock pulverization. Use of secondary susceptors such as β-SiC provides general method to elevate the temperatures of materials which then couple with microwaves at higher temperatures.

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