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Sintering of vanadium-doped magnesium oxide

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Abstract

This work presents sintering experiments of MgO doped with 0.025 to 2 cat% vanadium. Low levels of dopant were chosen to avoid the formation of a network of secondary phases in the final microstructure. Dense MgO ceramics (99.5%) were obtained with only 0.05 cat% vanadium, added as magnesium-vanadate to the MgO-powder, at sintering temperatures as low as 1250 °C.

Keywords: Doping; Liquid phase sintering; $Mg_3V_2O_5$; MgO; Substrate; Tape-casting; Vanadium

1. Introduction

For the application of MgO ceramics as substrate for melt-processing of Bi-2212 superconducting thick films, two microstructural features are essential: the MgO ceramic must have closed porosity and inertness towards the cuprate-melt. In addition, a percolating second phase should be avoided in order to minimize chemical attack of the substrate by the melt and to avoid contamination of the cuprate-melt by second phases of the substrate. Small amounts of secondary phase locally isolated may be tolerable.

Sintering of high purity magnesium oxide has been extensively studied.[1,2] Coble[3] summarized these experiments: “high-purity MgO does not exhibit significant densification at temperatures up to 1600 °C” and pointed out the important effects of impurities and atmospheric variables like water and carbon dioxide on the microstructural evolution of MgO during sintering.

The effect of various anion impurities and dopants on the densification behavior was studied by Hamano et al.[4] Additions of 5 wt% of a magnesium compound [$MgCl_2$, $Mg(NO_3)_2$ and MgC_2O_4] added to pure MgO, were found to enhance sintering and increase the final density, whereas $Mg(CH_3COO)_2$, $MgCO_3$ and $MgSO_4$ resulted in densities not higher than that of undoped magnesium oxide.

Transparent polycrystalline magnesium oxide was prepared by adding fluorine and chlorine to reagent grade MgO and $Mg(OH)_2$ starting powders.[5] Densification of isostatically pressed samples started at 1000 °C and transparent discs were obtained after a sintering time of 1 h at 1600 °C. Critical parameters in this process are the powder calcining temperature and the grain size: for grain sizes above 150 nm, doping had no effect on densification, independent of the amount added (0.02–4 wt.%).

Several cations with a beneficial effect on the densification of MgO have been found. The most extensive studies on this topic are those of Nelson and Cutler,[6] Layden and McQuerrie[7] and Matsumoto and Kato.[8]

Nelson and Cutler found enhanced sintering for TiO_2 at 1400 °C and for ZrO_2 at 1600 °C, but the effects were rather small. For additions in excess of 1–2 mol% TiO_2 and ZrO_2 they noticed the formation of secondary phases.

Layden and McQuerrie[7] selected 14 metal compounds as additives to magnesium carbonate prior to calcination, in concentrations of 0.1, 0.5 and 1 mol%. Two sets of samples were reported: one sintered for 2 h at 1225 °C (heating rate-120 °C/h) and the other sintered for 2 h at 1525 °C (heating rate 250 °C/h). The most effective dopants at 1225 °C were Li, Si, Ti, V, Mn, Fe. An addition of 0.5 mol% V led to a relative fired density of 90%, as compared to 58% for undoped samples. Ti, V, Zr and Ta were most effective for a sintering temperature of 1525 °C. Best results were obtained for additions

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of 1 mol% Ta, it enhanced the relative fired density from 91% for undoped samples to 96%. For vanadium doped samples, Layden and McQuerrie[7] reported the formation of a liquid during sintering at 1525 °C; however, relative densities of the sintered materials were only 94%.

Matsumoto and Kato studied mainly the effect of eight different oxide additions on the densification of vapor-phase synthesized (CVD) magnesium oxide. For comparison they included seawater magnesia in their study. One percent by weight of sintering aid was added and the samples heated for 1 h at 1500 °C. Samples with Ti02 and Zr02 reached relative densities of 95%, whereas undoped samples had a relative density of only 72%. For CVD-MgO a remarkable grain growth was found when the relative density increased above ~95%, independent of the sintering temperature (1500–1800 °C).

Brown[9] studied sintering of MgO with vanadium doping. He reported that the addition of 0.01–0.1 mol% of vanadium promotes sintering of highly pure (99.999%) magnesium oxide in the temperature range of 1250 °C to 1450 °C. Relatively low final densities of ~90% after 1 h at 1450 °C for 0.1 cat% V, and ~83% after 40 h at 1450 °C for 0.01 cat% V were found.

In a related work, Nicholson[10] reported electrical conductivity measurements in MgO samples doped with 0.1, 1, and 2 cat% V. In samples containing 1 and 2 cat% V he found a sudden increase in conductivity at 1200 °C and attributed this to the formation of a liquid phase. He studied also the lattice constant of the cubic periclase phase in doped and undoped samples in search for any solid solution. No significant change of the lattice parameter was observed and Nicholson concluded that there was little or no solid solution.

The aim of our work was to evaluate vanadium as a dopant for sintering magnesium oxide to high relative densities at low temperatures. Moreover, the additive should not form a continuous network of a secondary phase in the sintered ceramic. In view of the earlier results, significant enhancement of sintering due to the addition of vanadium was expected, but the minimum doping concentration was to be determined.

2. Experimental

2.1. Preparation of doped MgO powders

Two different MgO powders were chosen as starting materials: M.A.F., N°1425 (Magnesite B.Y., NL-Schiedam) and MgO (ACS quality) from Alfa Aesar (Nr. 35442). Both qualities have a mean particle size of 0.2 μm and a low impurity level.

For adding vanadium oxide to the starting powders in concentrations from 2 cat% down to 0.025 cat%, three different approaches were employed in the course of this work.

The first samples were prepared by a simple solution process (SSP). Additions of 0.1, 0.25, 0.5 and 1 cat% vanadium were made by preparing a solution of ammonium metavanadate ($NH_4 VO_3$, Nr. 1030, purum, Fluka) in water and adding the fine grained MgO powder while stirring the suspension. Water was then evaporated at 120 °C and the powder calcined at 600 °C, during which the dopant decomposed to V_2O_5, However, sintered samples of this powder showed clear evidence for inhomogeneous distribution of the additive in the MgO matrix.

To improve the dopant homogeneity, vanadium doped MgO with 0.1, 0.25, 0.5, 1 and 2 cat% vanadium was processed by dry ball milling of MgO (MAF) powder and vanadyl acetylacetonate (No. 81119, Alfa-Aesar). The latter compound melts at 260 °C and decomposes at higher temperatures. Calcination at 600 °C formed the desired V_2O_5 dopant. This process resulted in improved homogeneity of the dopant distribution as evidenced by the sintered samples and it will be referred to as volatile compound doping (VCD).

Still better homogeneity was found when the dopant was precipitated as $Mg_3V_2O_8$ in an alcoholic MgO slurry. This precipitation doping process (PDP) is based on the reaction of tetramethylammonium vanadate solution with magnesium nitrate in ethanol. The reaction product precipitates quantitatively from the solution. In the doping process, an ethanol based slurry of MgO is divided into two equal volumes. The desired amount of tetramethylammonium vanadate solution was mixed into one of them, the appropriate amount of magnesium nitrate solution into the other one. On combining both volumes under strong stirring, the precipitating compound distributes very homogeneously throughout the MgO suspension. After filtering and washing the powder with EtOH followed by acetone washing, the powder was dried and calcined at 400 °C for 2 h.

Precipitation doping was used for both MgO starting powders, M.A.F. No 1425 and Alfa Aesar's ACS quality. All powder mixtures prepared are summarized in Table 1.

Table 1
Powder mixtures of vanadium-doped MgO prepared in the course of this study

Starting powder	Doping process	Doping level (cat%)						
		0.025	0.05	0.1	0.25	0.5	1.0	2.0
MgO, ACS	PDP	X	X	X	X			
MgO M.A.F. No. 1425	PDP			X	X	X	X	X
	VCD			X	X	X	X	X
	SSP			X	X	X	X	

The precipitation process used for the preparation of doped MgO has also been used to prepare fine powders of the nominal composition $Mg_3V_2O_8$ and $Mg_5V_2O_{10}$. The only difference in the preparation was the use of two equal volumes of EtOH, with appropriate amounts of vanadate solution in one and magnesium nitrate solution in the other, followed by mixing them to effect precipitation.

2.2. Preparation of green bodies

Two sets of green bodies were prepared. Specimens for sintering in the dilatometer were made from isostatically pressed green bodies (250 MPa) by machining. The dimensions of these specimens were 5 mm in diameter and 5–10 mm in length.

Specimens for sintering experiments in a furnace were first axially pressed (150 MPa) then isostatically pressed at 250 MPa and had dimensions of 15 mm in diameter and 10 mm in height.

2.3. Tape casting

In view of the intended application of MgO ceramics as substrates for melt-processing of Bi-2212 thick films, tape casting of V-doped MgO was briefly explored. Green tapes were cast from a slurry prepared from MgO (MAP) + 1 cat% V (VCD) powder and from MgO (ACS) + 0.125 cat% V (PDP) powder. Details have been reported elsewhere.[11] The dried tapes were laminated by pressing symmetrical stacks of two and four tapes. Binder burn out was done by slow heating at 1 °C/min to 400 °C under load to prevent warping.

2.4. Sintering study

All compositions of V-doped MgO used for the sintering studies are listed in Table 1. One set of samples was sintered in a dilatometer (Dilatometer 802S, 1600 °C SiC furnace, Bahr, D-Htillhorst) at a constant heating rate of 5 °C/min to 1600 °C. A second set was sintered isothermally at 1050, 1150, 1250, or 1350 °C. The heating rate to the selected temperature was 25 °C/min.

The set of specimens sintered in a high-temperature furnace was embedded in undoped MgO powder for good temperature homogeneity. The furnace was heated at 2 °C/min to 1250 °C and held there for 12 h in all experimental runs.

For comparison, isothermal sintering of both MgO undoped raw powders was studied at 1600 °C by dilatometry. Isostatically pressed samples were heated at a rate of 25 °C/min to 1600 °C and kept there for 20 h. In addition, samples of Mg O(MAF) were sintered in a conventional high-temperature furnace. Sintering was frequently interrupted and the sample density measured.

2.5. Thermal analyses

DTA (STA 501, Bahr, D-Htillhorst) was used to analyze phase transitions in doped magnesium oxide samples. The samples used for the DTA were pressed bodies of MgO (MAP) with 1 cat% vanadium doped by SSP.

Powders with the nominal composition of $Mg_3V_2O_8$ and $Mg_5V_2O_{10}$ have been evaluated by DTA to confirm the melting of $Mg_3V_2O_8$. Further the absence of Mg–V–O compounds above 75% MgO in the phase diagram was checked.

2.6. Microstructure

Optical microscopy as well as scanning electron microscopy were employed to analyze the microstructures of sintered samples. The average grain size was determined from equivalent diameters of at least 50 grains per sample.

Mercury intrusion porosimetry (Porosimeter 2000; CE Instruments, I-Milan) was used to determine the pore size distribution of green and sintered bodies in the range 10 μm down to 10 nm.

2.7. Green and sintered density

The density of green and sintered samples was determined by repeated measurements using the standard Archimedes' method with poly(ethylen glycol) (M = 300 g/mol) as fluid.

2.8. Phase analyses

Phase analysis was carried out by XRD (D-5000, Siemens) and SEM in combination with EDX [Zmax30, NORAN Instruments Inc., Middletown (WI), USA]. Standardless EDX analysis has also been used to estimate the vanadium solubility in periclase. Samples of MgO + 1 cat% V (VCD) have been sintered for 1 to 25 h at 1300 °C and analyzed with respect to secondary phases and vanadium solubility.

3. Results and discussion

3.1. Sintering of undoped MgO

The sintering of undoped MgO was investigated by dilatometry. For both types of starting powders, the onset of sintering was found at ~1300 °C.

The normalized densification rates in all steps during sintering are plotted versus density in Fig. 1. Data were obtained from isothermal sintering runs at 1600 °C.

The densification rates of both MgO powders may be compared quantitatively, following the analysis suggested

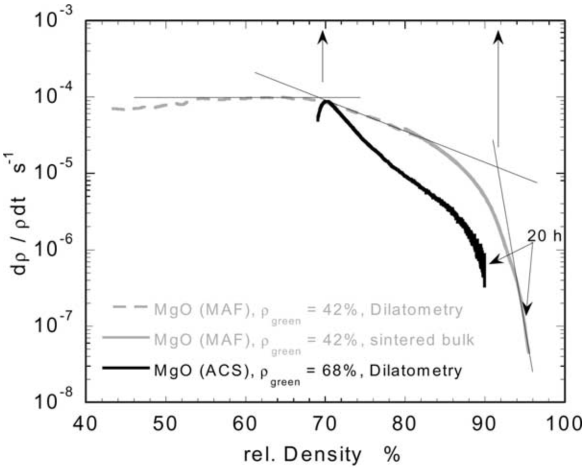


Fig. 1. Normalized densification rate versus relative density determined from isothermal sintering runs. Black line: MgO (ACS), grey line: MgO (MAF), data obtained from dilatometry ($<80\%$ rel. density) and density-measurements of sintered bulk samples ($>80\%$ rel. density).

by Chen.[12] It is based on the dimensionless argument first presented by Herring.[13] The normalized densification rate ($d\rho/\rho dt$) may be written as:

$$\frac{d\rho}{\rho dt} = F(\rho)\left(\frac{\gamma\Omega}{Gk T}\right)\left(\frac{\delta D}{G^3}\right) \quad (1)$$

Here, ρ is the relative density, t the time, γ the surface energy, Ω the atomic volume, G the grain size, δ the grain-boundary thickness, D the grain boundary diffusivity and F a dimensionless pre-factor.

In the case of the MgO (MAF) powder, the density increases at a relatively high but constant rate up to a relative density of 70%. Above 70% TD the shrinkage rate decreases to below 10^{-6} s^{-1}. To determine such small shrinkage rates, we measured the density of larger sintered bulk samples annealed in a furnace as described earlier. With relative densities approaching 96% the grain size increased to ~30 μm.

The first stage of sintering generally involves substantial particle rearrangement whereas above 70%, when grains are arranged in a closely packed manner, further densification requires grain boundary and volume diffusion. Above 92% TD, pores start to close and hinder further densification due to their inner gas pressure. During this third stage of solid state sintering (SSS), the densification rate decreases fast and grain growth is pronounced. For samples sintered 20 h at 1600 °C, the average grain size was 30 μm as compared to ~200 nm of the starting powder, hence the term $\delta D/G^3$ decreases fast and becomes rate determining. The final normalized densification rate of 10^{-7} s^{-1} as observed in these experiments corresponds to a densification of 1% within 30 h at a relative density of 95%—such samples won't sinter to full density ($>99\%$ TD).

Samples prepared from MgO (ACS) showed a different behavior. Their green density of 68% TD does not allow a significant densification by particle rearrangement, thus the first stage of SSS with a constant shrinkage rate as for the MgO (MAF) powder is not observed in these samples. Second stage sintering proceeds much slower than in case of the MgO (MAF) powder compacts, resulting in a density of 90% TD for MgO (ACS) powder compacts after 20 h sintering at 1600 °C, as compared to 95% TD for the MgO (MAF) powder compacts. In looking for a difference between the MgO (MAF) and the MgO (ACS) samples that may explain this different sintering behavior, it is noted that the most dominant difference is in the impurity content: the ACS powder contains 0.5 wt.% sodium, which is absent in the MAF material. Layden and McQuarrie found that "sodium appears to hinder densification at all concentrations".[7] We therefore assume that the much slower densification in the ACS powder is caused by the sodium impurity content.

In summary, high temperatures are required for the sintering of undoped MgO powders. Whereas powder compacts prepared from MgO (MAF) can be sintered to closed porosity within ~20 h at 1600 °C, powder compacts prepared from MgO (ACS) do not sinter to closed porosity despite the higher green density of these samples.

3.2. Sintering of V-doped MgO

We studied the densification of V-doped MgO by dilatometry for both MgO starting powders and doping levels of up to 0.25 cat% vanadium. Constant heating rate experiments showed, as mentioned before, that undoped MgO starts to sinter at ~1300 °C. An amount of 0.025 cat% V was found to have a rather small effect on densification. For higher amounts of dopant, 0.05 and 0.1 cat% V, samples sinter very fast in a narrow temperature window, beginning at ~1200 °C.

At a constant heating rate of 5 °C/min, samples of MgO (ACS) + 0.1 cat% V (PDP) start to densify at 1190 °C and their densification is completed at 1260 °C, taking 14 min altogether.

The effect of different doping levels on the densification kinetics can best be seen from $d\rho/\rho dt$ versus ρ plots, obtained from isothermal experiments, as shown in Fig. 2. For the ACS starting powder an addition of 0.025 cat% V does not enhance sintering at 1250 °C. Additions of 0.05 cat% V already accelerate sintering strongly, leading to fully dense samples ($>99\%$ TD) within 2 h sintering at 1250 °C. Even higher densification rates are obtained for 0.1 and 0.25 cat% V. Densification in those samples is very rapid and completed within less than 15 min at 1250 °C.

In order to study the influence of temperature, powder compacts with 0.05 cat% V were heated at 25 °C/min to sintering temperatures of 1050, 1150, 1250 and 1350 °C. At 1050 and 1150 °C, densification is much slower compared to that at 1250 and 1350 °C. Samples of MgO + 0.05 cat% V do not sinter to high densities at 1050 and 1150 °C. The normalized densification rate of the 1250 °C sintered material is constant up to a density of 95% TD. Higher sintering temperatures up to 1350 °C do not result in higher shrinkage rates.

In order to study the influence of the doping method, shrinkage rates were recorded from samples prepared by the SSP, VCD and PDP methods and plotted versus density in Fig. 3. Only those samples prepared by PDP reach high densities above 95% TD. For MgO (MAF) + 0.1 cat% V (PDP), a sintered density of 96% was found and for the similar doped MgO (ACS) + 0.1 cat% V the sintered density was 99.1%. The MgO (MAF) was also doped by SSP and VCD with 0.1 cat% V. These two doping methods were clearly inferior to the PDP, resulting in samples with sintered densities of 86% TD only for both methods.

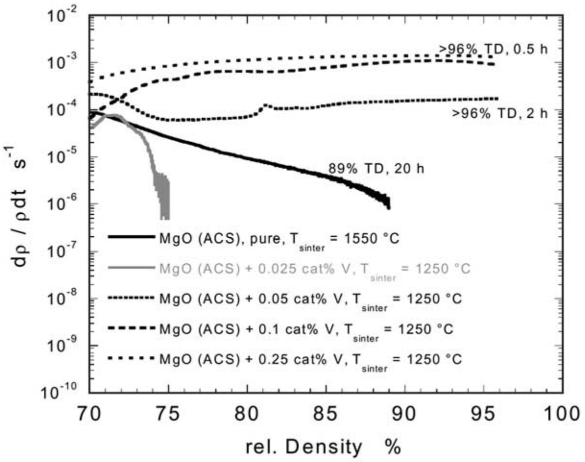


Fig. 2. Normalized densification rate versus relative density during sintering of pure and V-doped MgO (ACS). All samples pressed isostatically, ρ_{green}=68% TD.

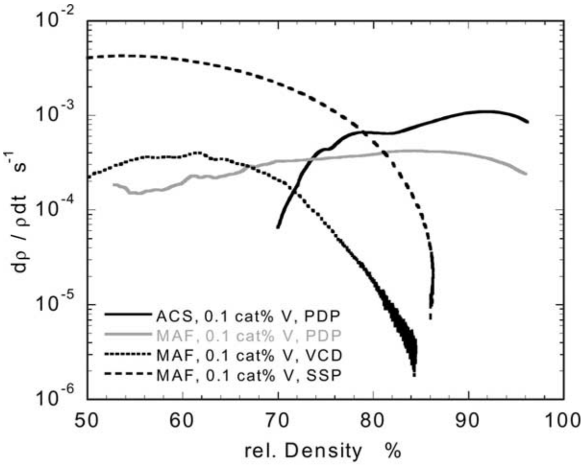


Fig. 3. Normalized densification rate versus relative density during sintering of 0.1 cat% V-doped MgO (ACS and MAF). All samples pressed isostatically and sintered at 1250 °C.

3.3. Sintered density

To explore the maximum density that can be reached for the different powder mixtures, four sets of samples were sintered with the same temperature program, applying a holding time of 12 h at 1250 °C. Each set was prepared by pressing cylinders from powders, derived from one particular MgO quality and doped with various vanadium concentrations by one of the three processes, SSP, VCD or PDP. The resulting final densities are plotted in Fig. 4 and Table 2 summarizes the densities after sintering. It is clearly seen that each set has its own peak in density occurring at a different dopant concentration. Even more significant is the observation how the maximum densities achieved in each set depends on the MgO quality and the homogeneous distribution of vanadium obtained by a particular doping process. Brown[9] used a method similar to our SSP to obtain MgO powders with 0.01–0.1 cat% V and obtained densities of 90% TD after 1 h sintering at 1450 °C for samples doped with 0.01 cat% V. The most remarkable result in the present work is the 99.5% relative density achieved for the samples MgO (ACS) doped with only 0.05 cat% vanadium by PDP. Comparable results for MgO ceramics, sintered pressureless at 1250 °C, have not been reported before.

3.4. Microstructural evolution

Pore size distributions of both green and sintered bodies were measured by mercury intrusion porosimetry. The specific pore volume versus pore radius plots of green bodies prepared from the two MgO starting powders are shown in Fig. 5. Average pore radii were 40 nm for the ACS and 64 nm for the MAF greenbodies. Since densification of samples with 0.1 cat% V and above proceeds at very high rates, sintering of these samples cannot be interrupted in different

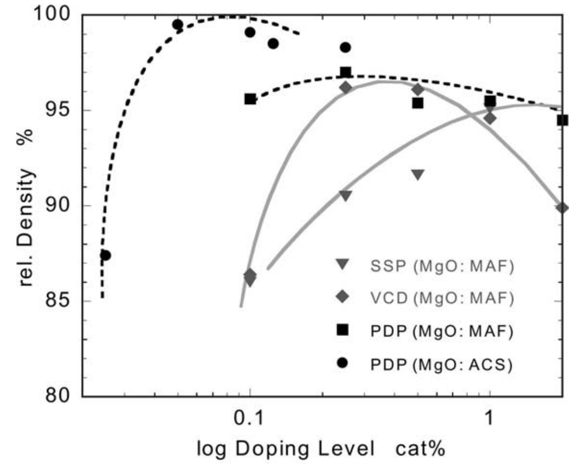


Fig. 4. Sintered densities after 12 h at 1250 °C. Lines are to guide the eye only.

Table 2
Sintered densities of vanadium-doped MgO samples

Starting powder	Doping process	Doping level (cat%)						
		0.025	0.05	0.1	0.25	0.5	1.0	2.0
MgOAlfa Aesar ACS	PDP	87.4	99.5	99.1	98.3			
	PDP			95.5	97	95.4	95.5	94.5
	VCD			86.0	96.2	96.0	94.5	90.0
MgO M.A.F. No. 1425	SSP			86.0 cracks	90.5 cracks	91.6	95.1	

The term "cracks" refers to samples that cracked regularly during sintering.

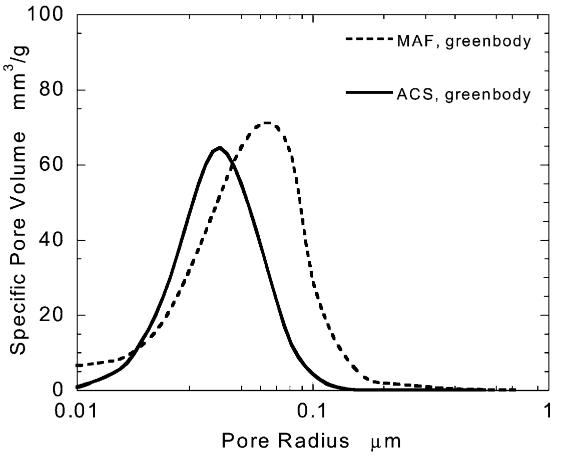


Fig. 5. Pore size distribution for MgO greenbodies. Relative densities are 52% for the MAF and 68% for the ACS powder compacts.

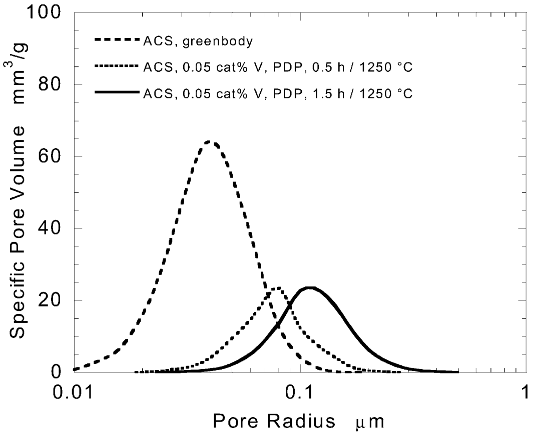


Fig. 6. Pore size distribution for samples of MgO (ACS) + 0.05 cat% V sintered for different times at 1250 °C. Relative densities for the 0.05 cat% V-doped samples were 67% (greenbody), 82% (0.5 h at 1250 °C) and 87% (1.5 h at 1250 °C).

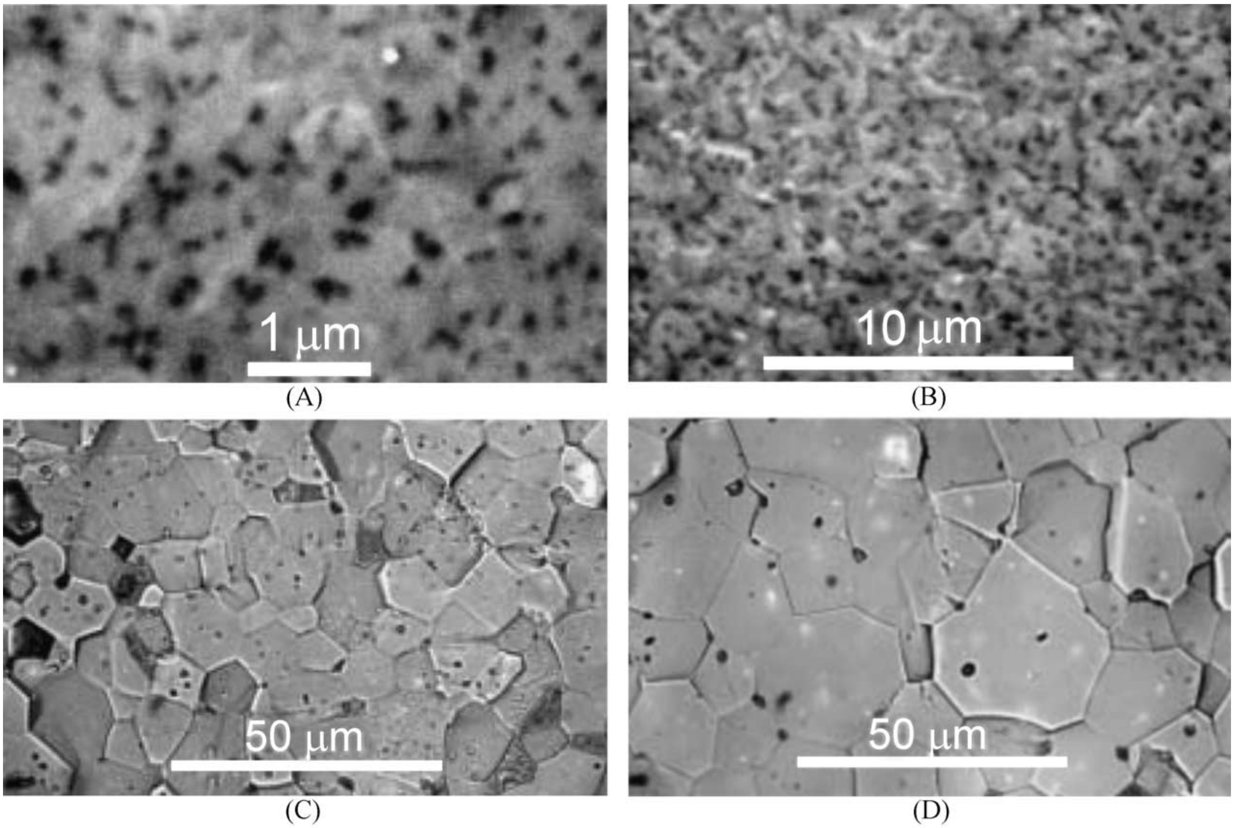
Table 3
Microstructural data for partially sintered samples of MgO (ACS) + 0.05 cat% V (PDP)

Rel. density (%)	Sintering time at 1250 °C	Grain size (µm)	Pore radius (nm)
68 ± 1	Greenbody		40
70 ± 1	1 min		
82 ± 1	1 h		80
87 ± 1	1.5 h		110
>99	2 h	10	
>99	4 h	18	

stages. In contrast, densification rates in MgO (ACS) + 0.05 cat% V (PDP) are sufficiently slow (full density is achieved after approximately 2 h at 1250 °C) that sintering of these samples can easily be interrupted and the microstructure be characterized at different relative densities. Fig. 6 shows the development of the pore size distribution for such samples. The average pore size increases as sintering and densification proceeds. The average pore radii were 80 nm for the sample sintered to 82% TD and 110 nm for the 87% TD sample. The microstructure of these samples could be resolved by scanning electron microscopy, confirming the porosimetry data. Grain and pore sizes for partially sintered MgO (ACS) + 0.05 cat% V (PDP) samples are summarized in Table 3. Dense samples show an average grain size of 10–20 µm, depending on the sintering time. Fig. 7 shows micrographs for samples sintered 1, 2, and 4 h at 1250 °C. The microstructures indicate that the pronounced grain growth takes place in the very last stage of sintering.

3.5. Phase analyses

In order to identify the phases present after sintering, samples were evaluated by XRD. Fig. 8 shows the diffraction patterns for samples prepared by PDP of MgO (ACS) and for MgO (M.A.F.) powder doped with solutions of ammonium metavanadate. Specimens doped with ⩾0.25 cat% V were found to contain at least one second phase. This second phase could not be identified by comparison with JCDD data. Precipitation doped samples with 0.025, 0.05, and 0.1 cat% V were found to be free of a second phase by XRD. Comparison of the pattern for MgO (ACS) doped with 0.25 cat% V by PDP and MgO (MAF) doped with solutions of ammonium metavanadate indicates that the raw powder as well as the doping process influence the phase composition after sintering. Peaks of a second phase are difficult to detected and could not be identified in the precipitation doped sample. However, firm conclusions cannot be drawn from this evidence alone, because the maximum amount of $Mg_3V_2O_8$, which is the Mg–V–O



(A) (B) (C) (D)

Fig. 7. Secondary electron and optical micrographs of MgO (ACS) + 0.05 ca 1% V. Polished cross-sections. A: SEI of a greenbody, relative density 68%. B: SEI of a sample sintered for 1 h at 1250 °C, relative density 82%. C: Optical micrograph of a dense sample (> 99% TD) sintered for 2 h at 1250 °C, average grain size 10 μm. D: Optical micrograph of a dense sample (> 99% TD) sintered for 4 h at 1250 °C, average grain size 18 μm.

compound richest in Mg, is less than 1 vol% and may escape conclusive detection.

DTA has been used to detect the presence of any phases undergoing a transformation upon heating or cooling after annealing at high temperatures. Samples were annealed in a DTA, cooled down and reheated, both at 25 K/min, after 1, 2, 4, 8, 16, and 24 h. Upon heating, endothermic reactions were observed at 1150 °C for all annealing times at 1300 °C. Exothermic reactions upon cooling occurred between 1140 °C and 1120 °C. A second exothermic reaction upon cooling was found at 990 °C. These experiments showed that extended annealing times at 1300 °C are not effective to dissolve the secondary phase(s) formed in samples doped with 1 cat% V and indicate a very small solubility of V^{5+} in the MgO lattice, far below the 1 cat% present in the samples studied by DTA.

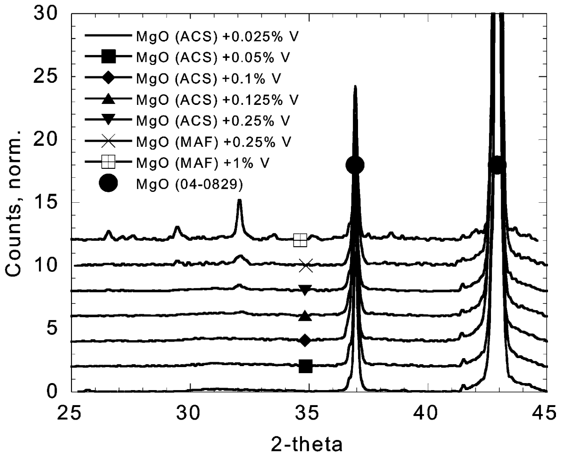


Fig. 8. XRD pattern of V-doped MgO.

Neither from XRD nor DTA of the doped samples it is possible to identify the secondary phase(s). In order to clarify the composition of the liquid phase, samples of the nominal composition of $Mg_3V_2O_8$ and $Mg_5V_2O_{10}$ have been prepared by coprecipitation and evaluated by DTA and XRD. After calcination, powders with the nominal composition $Mg_5V_2O_{10}$ consisted only of the periclase phase and the $Mg_3V_2O_8$ phase, which is in agreement with.[14] DTA detected an endothermic reaction at 1190 °C upon heating and an exothermic reaction at 1190 °C upon cooling. No other reactions were seen in these experiments. The $Mg_3V_2O_8$ nominal sample contained minor amounts of $Mg_2V_2O_7$. Upon heating, endothermic reactions were found at 884, 1090, and 1180 °C. Upon cooling, exothermic reactions were detected at 1180, 990, 873 and 645 °C. From these experiments, we assume the melting temperature of

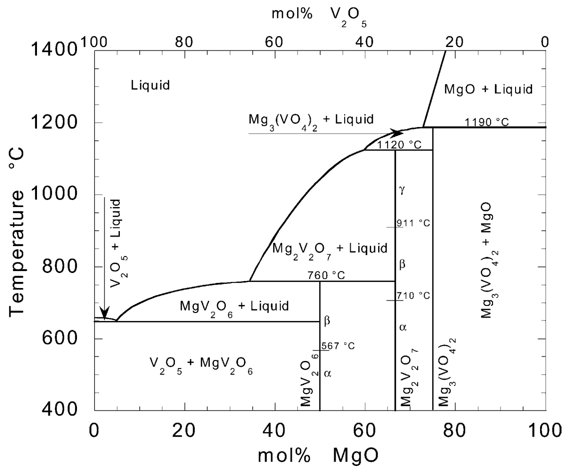


Fig. 9. Tentave phase-diagram V_2O_5–MgO. Based on the data of Clark and Morley[14] and of Kerby and Wilson.[15] Markers indicate polymorphic transitions.

$Mg_3V_2O_8$ to lie between 1180 and 1190 °C. The melting temperature of the $Mg_3V_2O_8$ phase is close to the temperature of the endothermic reactions detected when heating samples of MgO + 1 cat% V, thus we suspect the liquid accelerating sintering in our samples to be of the composition $Mg_3V_2O_8$ Much of the thermodynamic data published on the MgO–V_2O_5-system[14–16] is contradictory. However, we used these data to draw a tentative phase diagram of the MgO–V_2O_5-system, shown in Fig. 9. Clark and Morley[14] found three compounds in the system, $Mg_3V_2O_8$, $Mg_2V_2O_7$ and MgV_2O_6. We did only include these compounds in the diagram and left out all other phases that were not verified in their work.

This diagram is especially helpful in understanding the exothermic reactions seen in the cooling curve of the $Mg_3V_2O_8$ sample. Several transitions in the MgO–V_2O_5 system have been reported to be gradual in nature, it is plausible to assume that the formation of the solid $Mg_xV_yO_z$ phases upon cooling in the DTA is not complete and residual V-rich liquid persists down to the eutectic temperature.

We therefore assume that the action of the $Mg_3V_2O_8$-doping on the sintering of MgO is based on the formation of a liquid that wets the magnesia and assists in particle rearrangement during the first stage of sintering. During the second stage, fast material transport by way of the wetting liquid and dissolution or decomposition of MgO and the impurities in the reactive flux, promote sintering.

4. Summary

Magnesium oxide has been doped with small amounts of vanadiumoxide to enhance sintering. A liquid is formed at 1190 °C with the approximate composition of $Mg_3V_2O_8$ which promotes densification of the ceramic bodies. The influence of the amount of dopant, the doping method, and the annealing time and temperature on the final properties have been studied.

MgO doped with 0.05 cat% V, precipitated as $Mg_3V_2O_8$, was sintered to theoretical density within 2 h at 1250 °C with a final grain size of 10 μ. This work presents for the first time MgO ceramics sintered to theoretical density at ambient pressure.

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