

Microwave-assisted Acid Dissolution of Sintered Advanced Ceramics for Inductively Coupled Plasma Atomic Emission Spectrometry

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The microwave-assisted acid dissolution of sintered bodies of 28 structural and electronic advanced ceramic materials was systematically evaluated. These materials included zirconia-based ceramics, such as m-ZrO₂ (a non-stabilized monoclinic zirconia), Ca-PSZ and Mg-PSZ (two partially stabilized zirconias), Y-FSZ (a fully stabilized zirconia) and Ce-TZP, Yb-TZP and Y-TZP/Ce (three tetragonal polycrystalline zirconias); alumina-based ceramics, such as Al₂O₃, mullite and spinel; ceria-based ceramics, such as CeO₂-Gd₂O₃ (cubic ceria gadolinia); titania-based ceramics, such as TiO₂; titanate-based ceramics, such as Al₂TiO₅, BaTiO₃ and BIT (bismuth titanate); lead titanate-based ceramics, such as Ca-PT, La-PT, Nd-PT, Sm-PT and Gd-PT; lead zirconate titanate-based ceramics, such as PZT and PLZT; niobate-based ceramics, such as PMN (lead magnesium niobate); non-oxide-based ceramics, such as AlN, BN, Si₃N₄ and SiC; and oxide and non-oxide-based ceramics, such as β'-sialon (silicon aluminium oxynitride). Fifteen acids or mixtures of acids were tried, including HCl, HNO₃, H₂SO₄, *aqua regia*, H₂SO₄-(NH₄)₂SO₄ and mixtures of these acids with HF and with H₂O₂. A commercially available laboratory medium pressure microwave oven was used. Eleven optimized microwave methods were developed. These methods are simple (three stages maximum), fast (15–35 min digestion time) and mild (20–60% of the microwave oven power). By applying these microwave methods, it was possible to dissolve completely all the sintered advanced ceramics, except SiC and β'-sialon. These two non-oxide ceramics were the only samples that could not be dissolved by any of the acids or mixtures of acids tested. The microwave-assisted acid dissolution was compared for ICP-AES with conventional dissolution procedures, *i.e.*, alkali fusion in a platinum crucible and in a graphite crucible and acid decomposition by conductive heating at elevated pressure (in a PTFE bomb). It was demonstrated that microwave-assisted dissolution presents many advantages over the other procedures. When compared with acid decomposition by conductive heating in a PTFE bomb, one of the most important advantages is the drastic shortening of the digestion time from hours to minutes. When compared with alkali fusions, one of the most important advantages is the use of smaller amounts of high-purity acids, which contain less impurities than the fluxes; because of this, matrix effects and contamination from the attack reagents are lower, and consequently there is an improvement in the analytical figures of merit of ICP-AES.

Keywords: Microwave-assisted dissolution; structural sintered advanced ceramics; electronic sintered advanced ceramics; inductively coupled plasma atomic emission spectrometry

The terms advanced, engineering or technical ceramics refer to ceramic materials which exhibit superior mechanical proper-

ties, high-temperature stability, high-temperature strength, wear resistance, corrosion/oxidation resistance, chemical inertness, or electrical, optical and/or magnetic properties.¹

These materials are used in structural applications (machine and cutting tools, wear components, heat exchangers, aerospace components, automotive engine components such as turbocharge rotors and roller cam followers, power generation components, biomedical implants, processing equipment used for fabricating a variety of polymer, metal and ceramic parts) and in electronic applications (insulators, capacitors, actuators, transducers, varistors, electronic sensors and devices, oxygen sensors, temperature sensors, electrooptical elements and magnetic devices). In this way, the advanced ceramic materials can be classified into structural ceramics and electronic ceramics. These ceramics include binary oxide-based materials, such as alumina (Al₂O₃), zirconia (ZrO₂), titania (TiO₂) and ceria (CeO₂); ternary oxide-based materials, such as mullite (3Al₂O₃·2SiO₂), spinel (MgO·Al₂O₃) and aluminium titanate (Al₂TiO₅); non-oxide-based materials, such as boron nitride (BN), aluminium nitride (AlN), silicon nitride (Si₃N₄) and silicon carbide (SiC); perovskite-based materials, such as barium titanate (BaTiO₃), alkaline earth or rare earth element-modified lead titanate (*e.g.*, Ca-PT or Gd-PT), lead zirconate titanate or PZT (PbZr_{1-x}Ti_xO₃) and lanthanum-modified lead zirconate titanate or PLZT (Pb_{1-y}La_yZr_{1-x}Ti_xO₃); and oxide and non-oxide mixed compounds, such as silicon aluminium oxynitride or β'-sialon (Si_{6-x}Al_xO_xN_{8-x}), a set of materials based on combinations of Si₃N₄ with Al₂O₃ and other oxides.

The properties of these materials are greatly influenced by the stoichiometric molar ratio of the macroconstituents,² and also by the presence of impurities,³ even at very low concentrations. Furthermore, small amounts of dopants,⁴ sintering aids⁵ and other additives⁶ are added to these ceramics in order to improve their processing and ultimate properties. Because of this, the determination of these elements is vital to manufacturing control, property improvement, failure prevention and quality assurance.

Inductively coupled plasma atomic emission spectrometry (ICP-AES) is nowadays the most widely used technique for the analytical characterization of advanced ceramics. It has been applied to the chemical analysis of a wide variety of samples: Al₂O₃,^{7–10} ZrO₂-based materials,^{11–14} AlN,^{9,10,12} Si₃N₄,^{9,10,15–17} SiC,^{9,10,18–20} perovskite-based materials,^{13,21} BaTiO₃,^{13,22,23} Gd-PT,¹³ PZT,^{13,24} PLZT,¹³ *etc.* For the chemical analysis of these refractory and chemically resistant materials, complete dissolution of the samples with extreme chemical treatments must be performed. This has been realized by two general procedures: acid decomposition and alkali fusion. Acid decomposition procedures include: (i) conductive heating at atmospheric pressure with H₂SO₄+HF in a platinum dish,²⁵ HCl+H₂SO₄+HF in a platinum crucible,¹⁴ H₂SO₄+(NH₄)₂SO₄ in a glass beaker^{11–13,24,26} or a platinum dish^{13,21}

and $\text{H}_3\text{PO}_4 + \text{H}_2\text{SO}_4$ in a quartz beaker,⁷ a PTFE beaker⁸ or a platinum crucible,²⁷ and (ii) conductive heating at elevated pressure with HCl ,^{8,12,13,21-23,25,28-31} HNO_3 ,³² H_2SO_4 ,²⁸ $\text{HCl} + \text{HNO}_3$,^{9,10} $\text{HCl} + \text{H}_2\text{SO}_4$,^{9,10,32,33} $\text{H}_2\text{SO}_4 + \text{HClO}_4$,²⁸ $\text{H}_2\text{SO}_4 + \text{H}_3\text{PO}_4$,²⁸ HF ,^{28,34} $\text{HCl} + \text{HF}$,^{35,36} $\text{HNO}_3 + \text{HF}$,^{9,10,17,37,38} $\text{H}_2\text{SO}_4 + \text{HF}$,^{13,21,24,28} $\text{HClO}_4 + \text{HF}$,²⁸ $\text{H}_3\text{PO}_4 + \text{HF}$,²⁸ $\text{HCl} + \text{HNO}_3 + \text{HF}$,²⁶ $\text{HNO}_3 + \text{H}_2\text{SO}_4 + \text{HF}$,^{9,10,19,20,33,39,40} and $\text{HF} + \text{H}_2\text{O}_2$ ³² in a PTFE bomb. Alkali fusion procedures include: (i) fusion in a platinum crucible with Na_2CO_3 ,^{23,41} $\text{Na}_2\text{CO}_3 + \text{Na}_2\text{B}_4\text{O}_7$,^{12,13,21} $\text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4$,¹⁵ $\text{Na}_2\text{B}_4\text{O}_7 + \text{KNO}_3$,⁴² $\text{CaCO}_3 + \text{H}_3\text{BO}_3$,²⁵ $\text{Li}_2\text{CO}_3 + \text{H}_3\text{BO}_3$ ⁷ and $\text{Na}_2\text{B}_4\text{O}_7 + \text{H}_3\text{BO}_3 + \text{LiOH}$,⁴³ and (ii) fusion in a graphite crucible with LiBO_2 ⁸ and $\text{Li}_2\text{B}_4\text{O}_7$.^{13,21,23,24} For comparative purpose, Table 1 summarizes the literature methods using acid decomposition by conductive heating at elevated pressure in a PTFE bomb for the dissolution of advanced ceramic powders.

However, these dissolution procedures, which are a major source of errors and difficulties, present several serious disadvantages. Acid decomposition procedures are time consuming, often require the use of potentially hazardous acids and can lead to systematic errors such as contamination, loss of volatile elements and incomplete digestions. Alkali fusion procedures, although efficient and relatively rapid, are very laborious, requiring constant supervision during operation, and can also

lead to the aforementioned systematic errors. In addition, the high reagent blank of the fluxes and the large dilution factor of the sample solution can lead to a decrease in the sensitivity.

The microwave-assisted heating technique^{44,45} is a promising alternative for sample preparation owing to the advantages over the conventional acid decomposition and alkali fusion procedures: strict control of the heating power and of the time the heating is applied, more amenable to automation, ability to use small volumes of reagents, lower reagent blank, complete digestion without the use of HClO_4 , extremely short digestion times, lower risk of contamination from the decomposition vessel and from the laboratory environment, no losses of volatile elements, *etc.*

Despite the great interest that this technique presents, only two papers^{32,46} devoted to their application to ceramic materials could be found. Table 2 summarizes the microwave-assisted dissolution methods used in these papers. Tatár *et al.*⁴⁶ studied the influence of various physico-chemical properties (crystalline phase, particle size and specific surface area) of Al_2O_3 samples on efficiency of microwave-assisted digestion with H_2SO_4 (1+1) at 170 °C as a function of time. Matusiewicz³² compared a commercial microwave-assisted digestion system with the conventional PTFE bomb decomposition for the dissolution of Al_2O_3 , AlN , BN and Si_3N_4 samples. However, all the samples in both studies were commercial

Table 1 Summary of literature methods using acid decomposition by conductive heating at elevated pressure in a PTFE bomb for the dissolution of advanced ceramic powders

Ceramic powder	Sample mass/ mg	Acid or mixture of acids/ ml	Temperature/ °C	Time/ h	Ref.
ZrO_2	1000	15 HF	190	8	34
	600	12.5 H_2SO_4 + 12.5 HF	240	4	28
	100	1 HCl + 0.3 HNO_3 + 4 HF	120	2	26
Al_2O_3	—	HCl	215	16	8
	1000	10 HCl	240	6	31
	500	15 H_2SO_4 (with agitation)	240	3	28
	1000	10 HCl + 1 H_2SO_4	230	6	9
	700	10 HCl + 1 H_2SO_4	230	6	10
	100	3 HCl + 2 H_2SO_4	200	24	32
	1000	10 HCl + 1 H_2SO_4	225	6	33
	500	5 H_2SO_4 + 5 H_3PO_4 (with agitation)	240	4.5	28
	500	15 HF (with agitation)	240	3.5	28
	500	15 HF + 3 HClO_4 (with agitation)	240	3.5	28
	Mullite	400	10 H_3PO_4 + 5 HF	240	6
Spinel	300	12 H_2SO_4 + 1 HClO_4	240	10	28
AlN	200	5 HCl	160	12	12
	100	HCl	230	12	30
	100	3 HNO_3	180	2	32
	760	6 HCl + 2 HNO_3	220	4	9
	760	9.5 HCl + 2 HNO_3	220	4	10
BN	30	4 H_2SO_4	240	6	28
	100	3 HF + 0.5 H_2O_2	180	5	32
Si_3N_4	60	1.5 HCl + 1.5 HF	150	>7	35
	145–660	1 HNO_3 + 3 HF	150	>12	38
	400	1.5 HNO_3 + 2 HF	180–200	10	37
	250	3 HNO_3 + 6 HF	200	6–8	17
	250	1.8 HNO_3 + 5 HF	220	4	9
	250	1.8 HNO_3 + 5 HF	220	4	9
SiC	100	3 HF + 0.5 H_2O_2	180	6	32
	250	4 HNO_3 + 4 H_2SO_4 + 4 HF	240	8–20	19
	200	4 HNO_3 + 3.5 H_2SO_4 + 4 HF	250	5	10
	250	4 HNO_3 + 4 H_2SO_4 + 4 HF	250	12	33
SrTiO ₃	250	4 HNO_3 + 4 H_2SO_4 + 4 HF	250	12	40
	300	25 HCl	240	2	28
BaTiO ₃	100	10 HCl + a few ml of HF	200	4	36
	50	15 HCl	150	16	22
	200	5 HCl	160	14	23
	200	5 HCl	160	16	13
Gd-PT	300–500	25 HCl	240	4	28
	200	5 HCl	160	16	13
PZT	200	0.4 H_2SO_4 + 2 HF	170	16	13
	200	0.4 H_2SO_4 + 2 HF	170	16	24
PLZT	200	0.4 H_2SO_4 + 2 HF	170	16	13

Table 2 Summary of literature methods using acid decomposition by microwave-assisted heating at elevated pressure for the dissolution of advanced ceramic powders

Ceramic powder	Sample mass/mg	Acid or mixture of acids/ml	Stage 1		Stage 2		Total time/min	Ref.
			Time/min	Power/W	Time/min	Power/W		
Al ₂ O ₃ (0% α -phase)	200	10 H ₂ SO ₄	3	630	5	315	8	46
Al ₂ O ₃ (17.1% α -phase)	200	10 H ₂ SO ₄	3	630	120	315	123	46
Al ₂ O ₃ (43.6% α -phase)	200	10 H ₂ SO ₄	3	630	120	315	123	46
Al ₂ O ₃ (96.1% α -phase)	200	10 H ₂ SO ₄	3	630	240	315	243	46
Al ₂ O ₃ (98.4% α -phase)	200	10 H ₂ SO ₄	3	630	420	315	423	46
Al ₂ O ₃ (100% α -phase)	200	10 H ₂ SO ₄	3	630	240	315	243	46
Al ₂ O ₃ (100% α -phase)	200	10 H ₂ SO ₄	3	630	360	315	363	46
Al ₂ O ₃	100	3 HCl + 2 H ₂ SO ₄	5	250	15	500	20	32
AlN	100	3 HNO ₃	5	250	10	500	15	32
BN	100	3 HF + 0.5 H ₂ O ₂	5	250	10	500	15	32
Si ₃ N ₄	100	3 HF + 0.5 H ₂ O ₂	5	250	10	500	15	32

powders of micron and submicron particle size. Such types of powders are generally used as starting materials in the preparation of ceramics. Therefore, they cannot really be considered as ceramic materials, since ceramic materials are formed from non-metallic polycrystalline inorganic compounds having been, as a common feature, consolidated from a powder by thermal treatment at high temperatures (the so-called sintering process).

The aim of this work was to develop methodologies for the microwave-assisted dissolution of sintered bodies of a great variety of structural and electronic advanced ceramic materials for their reliable chemical analysis by ICP-AES, and to compare them with well established conventional acid decomposition and alkali fusion procedures. Another purpose was to evaluate the influence of sample solutions obtained by the different dissolution methods on the analytical figures of merit of ICP-AES.

EXPERIMENTAL

Instrumentation

Microwave digestion system

A commercially available laboratory medium pressure microwave oven (RMS-150 remote microwave-digestion system; Floyd, Lake Wyle, SC, USA) operating at a frequency of 2450 MHz with an energy output of 0–600 W adjustable in 1% increments from 0 to 100% was used to perform the acid digestions. The microwave system, featuring programmable time and power (24 stage programming, 100 programme storage), consists of an oven, an extraction fan, a remote control console, a rotating turntable and 12 digestion closed vessels (80 ml capacity), each of which is connected by a venting tube to a central waste container. The digestion vessels, made from perfluoroalkoxy (PFA), incorporate a double-wall design and use disposable PFA rupture discs to ensure safe operation up to a precise pressure limit of 1380 kPa.

ICP atomic emission spectrometer

Simultaneous multi-element determinations of the analytes in sample solutions were carried out with a Jobin-Yvon (Longjumeau, France) Model 70 Plus combination sequential-simultaneous ICP atomic emission spectrometer. The instrumentation and operating conditions were described in a previous paper.⁴⁷

Chemicals

Reagents

Analytical-reagent grade HCl (37%), HNO₃ (65%), H₂SO₄ (95–97%), HF (48%), H₂O₂ (30%), (NH₄)₂SO₄, Na₂CO₃,

Na₂B₄O₇ and Li₂B₄O₇ (Merck, Darmstadt, Germany) were used as reagents for dissolution procedures. De-ionized water with a resistivity >18 M Ω cm, produced by a Milli-Q Plus pure water generating system from Millipore (Bedford, MA, USA), was used for all solutions.

Standards

For ICP-AES measurements, mono-element stock standard solutions were purchased from Merck or Spex Industries (Edison, NJ, USA), or prepared from high-purity Specpure grade oxides (Johnson Matthey Chemicals, Royston, Hertfordshire, UK). From these solutions, calibration multi-element standard solutions were prepared by the serial dilution method. The different reagent blanks and the concomitant elements were also added to these standards.

Samples

All the advanced ceramic materials studied, which are specified in Table 3, were processed and sintered in the Instituto de Cerámica y Vidrio (Institute of Ceramics and Glass), Consejo Superior de Investigaciones Científicas (Superior Council of Scientific Research), Madrid, Spain.

By using mixed oxides or coprecipitated hydroxides as starting materials, green bodies were prepared by either isostatic pressing or slip casting. Subsequently, these green compacts were sintered by thermal treatment in the range 1400–1650 °C to obtain full dense pieces (cylindrical bars, 5–10 cm in length and 1–2 cm in diameter). In some materials, hot pressing at temperatures ranging from 1500 to 1550 °C was necessary to obtain the theoretical densities.

Sample Preparation

The full dense cylindrical bars of the sintered advanced ceramics were crushed and milled to a particle size below 20–30 μ m in a ball milling system. After this, a particle size below 5–10 μ m was obtained by using an attrition milling system. In order to minimize contamination, the composition of the balls used in both ball and attrition milling systems was similar to the composition of each sample (e.g., alumina balls were used for samples with high levels of aluminium such as Al₂O₃, mullite and spinel; zirconia balls were used for samples with high levels of zirconium such as m-ZrO₂, Ca-PSZ, Mg-PSZ, Y-FSZ, Ce-TZP, Yb-TZP, Y-TZP/Ce, PZT and PLZT).

Table 3 Sintered advanced ceramic materials used in the present work

Ceramic type	Name	Chemical formula	Abbreviation
Binary oxide-based	Non-stabilized monoclinic zirconia	ZrO ₂	m-ZrO ₂
	Alumina	Al ₂ O ₃	Al ₂ O ₃
	Titania	TiO ₂	TiO ₂
Ternary oxide-based	Calcium partially stabilized zirconia	ZrO ₂ -CaO	Ca-PSZ
	Magnesia partially stabilized zirconia	ZrO ₂ -MgO	Mg-PSZ
	Yttria fully stabilized zirconia	ZrO ₂ -Y ₂ O ₃	Y-FSZ
	Ceria tetragonal zirconia polycrystalline	ZrO ₂ -CeO ₂	Ce-TZP
	Ytterbia tetragonal zirconia polycrystalline	ZrO ₂ -Yb ₂ O ₃	Yb-TZP
	Cubic ceria gadolinia	CeO ₂ -Gd ₂ O ₃	CeO ₂ -Gd ₂ O ₃
	Mullite	3Al ₂ O ₃ · 2SiO ₂	Mullite
	Spinel	Al ₂ O ₃ · MgO	Spinel
	Aluminium titanate	Al ₂ TiO ₅	Al ₂ TiO ₅
	Bismuth titanate	Bi ₄ Ti ₃ O ₁₂	BIT
Quaternary oxide-based	Yttria ceria tetragonal zirconia polycrystalline	ZrO ₂ -CeO ₂ -Y ₂ O ₃	Y-TZP/Ce
Non-oxide-based	Aluminium nitride	AlN	AlN
	Boron nitride	BN	BN
	Silicon nitride	Si ₃ N ₄	Si ₃ N ₄
	Silicon carbide	SiC	SiC
Perovskite-based	Barium titanate	BaTiO ₃	BaTiO ₃
	Calcium-modified lead titanate	Ca _x Pb _{1-x} TiO ₃	Ca-PT
	Lanthanum-modified lead titanate	La _x Pb _{1-x} TiO ₃	La-PT
	Neodymium-modified lead titanate	Nd _x Pb _{1-x} TiO ₃	Nd-PT
	Samarium-modified lead titanate	Sm _x Pb _{1-x} TiO ₃	Sm-PT
	Gadolinium-modified lead titanate	Gd _x Pb _{1-x} TiO ₃	Gd-PT
	Lead zirconate titanate	Pb(Zr _{1-x} Ti _x)O ₃	PZT
	Lanthanum-modified lead zirconate titanate	Pb _{1-y} La _y (Zr _{1-x} Ti _x)O ₃	PLZT
	Lead magnesium niobate	Pb(Mg _{1/3} Nb _{2/3})O ₃	PMN
	Oxide and non-oxide mixed compound-based	Silicon aluminium oxynitride	Si _{6-x} Al _x O _x N _{8-x}

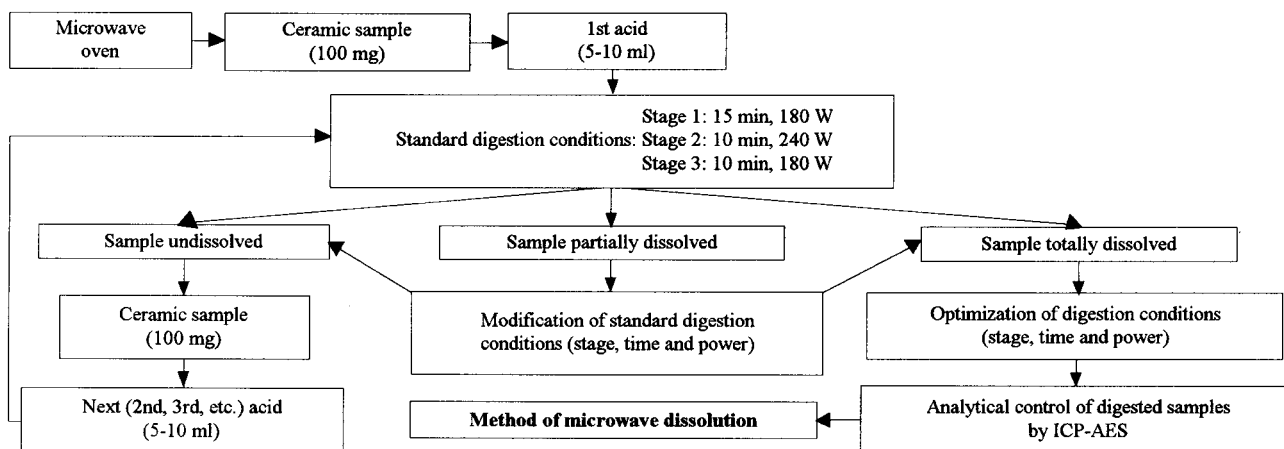


Fig. 1 Schematic diagram of the procedure for the microwave-assisted dissolution of the advanced ceramic materials.

Procedures

Sample dissolution by microwave-assisted digestion

A multi-step procedure, outlined in Fig. 1, was used. For each of the advanced ceramic materials, the acid or mixture of acids were used following the order given in Table 4, until full dissolution was obtained. About 100 mg of sample and 5–10 ml of the first acid in Table 4, HCl, were added, in duplicate, to the digestion vessels and were treated with the microwave standard digestion conditions indicated in Fig. 1 (stage 1, 15 min at 180 W; stage 2, 10 min at 240 W; and stage 3, 10 min at 180 W). Three situations could arise. (i) If the sample was not dissolved, that means that the powder remains (with the same aspect as it had before the treatment was applied); in this case, the sample was tested with the second acid in Table 4 (HNO₃). If the sample remained undissolvable, it was assayed with the next acid (H₂SO₄), and so on until it was dissolved. (ii) If the sample was partially dissolved or at least was attacked, that means that the powder has a different aspect to that of the initial powder; in this case, the standard digestion conditions were modified with respect to number of stages,

Table 4 Acids and mixtures of acids tested for the microwave-assisted dissolution of ceramic materials

Order	Acid or mixture of acids
1st	HCl
2nd	HNO ₃
3rd	H ₂ SO ₄
4th	HCl + HNO ₃ (3 + 1 v/v; <i>aqua regia</i>)
5th	(NH ₄) ₂ SO ₄ 20% m/v in H ₂ SO ₄
6th	HCl + HF
7th	HNO ₃ + HF
8th	H ₂ SO ₄ + HF
9th	HCl + HNO ₃ (3 + 1 v/v) + HF
10th	(NH ₄) ₂ SO ₄ 20% m/v in H ₂ SO ₄ + HF
11th	HNO ₃ + H ₂ SO ₄ + HF
12th	HCl + H ₂ O ₂
13th	HNO ₃ + H ₂ O ₂
14th	H ₂ SO ₄ + H ₂ O ₂
15th	HF + H ₂ O ₂

digestion time and/or microwave oven power, until the total dissolution of the sample was achieved. If total dissolution was not achieved, the same steps as the previous case must be applied. When total dissolution had been achieved, the next stage was applied. (iii) When the sample was completely dissolved, at least apparently, which means that a transparent solution appeared, the microwave digestion conditions (amounts of acids, number of stages, time and power of each stage) were optimized, checking accurately the amount of sample dissolved by means of the ICP-AES determination of the macro-constituents of the ceramic material. In this way, an improved method for the microwave-assisted dissolution of the ceramic material was created. The dissolved sample was completely transferred into a 100 ml calibrated flask and diluted to volume with water.

Sample dissolution by fusion with $\text{Li}_2\text{B}_4\text{O}_7$ in a graphite crucible

The sample (0.2000 g) was mixed with 2.00 g of $\text{Li}_2\text{B}_4\text{O}_7$ in a porcelain crucible and then quantitatively transferred into a graphite crucible. The mixture was fused in a muffle furnace at 1100 °C for 20 min. The melt was then carefully and quickly poured into a 400 ml glass beaker containing 100 ml of cold HNO_3 (1+24 v/v). The contents were stirred with a PTFE-covered magnetic bar on top of a magnetic plate until the melt dissolved. The solution was completely transferred into a 200 ml calibrated flask and diluted to volume with HNO_3 (1+24 v/v).

Sample dissolution by fusion with $\text{Na}_2\text{CO}_3 + \text{Na}_2\text{B}_4\text{O}_7$ in a platinum crucible

The sample (0.2000 g) was mixed with 2.00 g of $\text{Na}_2\text{CO}_3 + \text{Na}_2\text{B}_4\text{O}_7$ (53.7+46.3% m/m) in a platinum crucible and fused by heating on a Mekker burner for 30 min. The crucible was carefully introduced into a 250 ml glass beaker containing 100 ml of hot HCl (1+9 v/v) and gently heated until the fused sample was dissolved. The solution was completely transferred into a 200 ml calibrated flask and diluted to volume with HCl (1+9 v/v).

Determination of impurities in attack reagents by ICP-AES

Impurities of Ca, Fe, Mg, Si and Sr were determined by ICP-AES in the water and in the following acids used in the microwave-assisted dissolution of the sintered advanced ceramics: 5% HCl, 5% HNO_3 , 5% H_2SO_4 , 1% $(\text{NH}_4)_2\text{SO}_4$ and 5% $\text{H}_2\text{SO}_4 + 1\%$ $(\text{NH}_4)_2\text{SO}_4$. Also, the same elements were determined in the attack reagents (acids and fluxes) employed in the dissolution of the samples by fusion in a graphite crucible (4% HNO_3 and 4% $\text{HNO}_3 + 1\%$ $\text{Li}_2\text{B}_4\text{O}_7$) and by fusion in a platinum crucible (10% HCl, 0.54% Na_2CO_3 , 0.46% $\text{Na}_2\text{B}_4\text{O}_7$ and 10% HCl+0.54% $\text{Na}_2\text{CO}_3 + 0.46\%$ $\text{Na}_2\text{B}_4\text{O}_7$). The measurements were performed on the 393.366 nm line of Ca II, the 239.562 nm line of Fe II, the 279.553 nm line of Mg II, the 251.611 nm line of Si I and the 407.771 nm line of Sr II.

Determination of the detection limits of minor elements by ICP-AES

The detection limit was defined as the concentration which gave a net signal equal to three times the standard deviation of the background level (3σ). The determination of the detection limits for the most sensitive lines⁴⁸ of 16 elements (Table 5) was performed in solutions containing three different reagent blanks: (i) the blank corresponding to the hydrochloric acid microwave-assisted dissolution (5% HCl); (ii) the blank corresponding to the alkali fusion in a graphite crucible (4%

Table 5 Elements and emission lines used for the determination of detection limits

Element	Emission line/nm	Element	Emission line/nm
Ca II	393.366	Mn II	257.610
Ce II	413.765	Na I	589.592
Cu I	324.754	Nd II	415.608
Fe II	239.562	P I	213.618
Gd II	336.223	Si I	251.611
K I	766.490	Sm II	442.434
La II	408.672	Sr II	407.771
Mg II	279.553	Zr II	343.823

$\text{HNO}_3 + 1\%$ $\text{Li}_2\text{B}_4\text{O}_7$); and (iii) the blank corresponding to the alkali fusion in a platinum crucible (10% HCl+0.54% $\text{Na}_2\text{CO}_3 + 0.46\%$ $\text{Na}_2\text{B}_4\text{O}_7$). The influence of the major elements of each advanced ceramic material was not considered.

Chemical analysis of advanced ceramic materials

The chemical analysis of the advanced ceramic materials was carried out in triplicate for each dissolution method (acid microwave heating, alkali fusion with $\text{Li}_2\text{B}_4\text{O}_7$ in a graphite crucible and alkali fusion with $\text{Na}_2\text{CO}_3 + \text{Na}_2\text{B}_4\text{O}_7$ in a platinum crucible). The determination of the macro-constituents was performed on the 20-fold diluted sample solution. However, the determination of impurities was performed directly on the sample solution.

RESULTS AND DISCUSSION

The acids in Table 4 are those which have been most often used to dissolve advanced ceramic materials (Table 1). The acids are listed in order of increasing strength. In first place appear the acids alone, in second place the mixtures of these acids and in third place these acids and their mixtures with HF. In last place are also included powerful oxidizing mixtures (the previous acids in the presence of H_2O_2) which are effective in achieving the dissolution of several non-oxide-based ceramics (BN and Si_3N_4), as is inferred of Table 1. Since temperature cannot be measured in our microwave digestion system, HClO_4 was not used because a temperature can easily be exceeded without reaching the maximum pressure. Nevertheless, we included the mixture of $(\text{NH}_4)_2\text{SO}_4 + \text{H}_2\text{SO}_4$, which although it has not been used previously in attacks in a PTFE bomb, it has been employed with success in attacks in a beaker to dissolve ZrO_2 ,^{11,26} Y-TZP,¹² Gd-PT,¹³ PZT^{13,14} and PLZT,¹³ and also in attacks in a platinum dish to dissolve Ca-PSZ and Y-TZP/Ce.¹³

As can be seen when Tables 1, 2 and 3 are compared, only 12 of the 28 advanced ceramic materials tested in this work had been studied using acid dissolution in PTFE bomb, and only four of these 12 had been studied using microwave-assisted dissolution. Moreover, the samples studied in these earlier papers were not in fact ceramic materials, but commercial powders, generally of submicron particle size, which are used as raw materials for advanced ceramics manufacture. Any ceramic material is sintered by a high temperature treatment (1300–1700 °C or even higher), which is responsible for the formation of the ceramic material, which is a polycrystalline inorganic solid and which therefore always has a higher refractoriness and chemical inertness than the initial powders, and whose dissolution requires stronger conditions.

The results obtained after the attack of the 28 advanced ceramic materials in the microwave oven, with the acids in Table 4 and following the procedure in Fig. 1, are given in Table 6.

For the materials with high levels of zirconium, the mixture

Table 6 Results obtained in the microwave-assisted dissolution of the advanced ceramic materials

Ceramic material	Acid or mixture of acids*													
	HCl	HNO ₃	H ₂ SO ₄	HCl + HNO ₃	HNO ₃	HNO ₃ + HF	H ₂ SO ₄ + HF	HCl + HNO ₃ + HF	(NH ₄) ₂ SO ₄ + H ₂ SO ₄ + HF	HNO ₃ + H ₂ SO ₄ + HF	HCl + H ₂ O ₂	HNO ₃ + H ₂ O ₂	H ₂ SO ₄ + H ₂ O ₂	HF + H ₂ O ₂
m-ZrO ₂	-	-	-	+	-	-	-	-	-	-	-	-	-	-
Al ₂ O ₃	-	-	-	-	-	-	+	+	-	-	-	-	-	-
TiO ₂	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ca-PSZ	-	-	-	-	-	+	-	-	-	-	-	-	-	-
Mg-PSZ	-	-	-	-	-	-	+	-	-	-	-	-	-	-
Y-FSZ	-	-	-	-	-	+	-	-	-	-	-	-	-	-
Ce-TZP	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Yb-TZP	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Yb-TZP	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CeO ₂ -Gd ₂ O ₃	-	-	+	-	-	-	-	-	-	-	-	-	-	-
Mullite	-	-	-	+	-	-	-	-	-	-	-	-	-	-
Spinel	-	-	-	+	-	-	-	-	-	-	-	-	-	-
Al ₂ TiO ₅	-	-	-	-	-	-	+	-	-	-	-	-	-	-
BIT	-	-	-	-	-	-	+	-	-	-	-	-	-	-
Y-TZP/Ce	-	-	-	-	-	-	-	-	-	-	-	-	-	-
AlN	+	-	-	-	-	-	-	-	-	-	-	-	-	-
BN	-	-	-	-	-	-	-	-	-	-	-	-	-	+
Si ₃ N ₄	-	-	-	-	-	-	+	-	-	-	-	-	-	-
SiC	-	-	-	-	-	-	-	-	-	-	-	-	-	-
BaTiO ₃	+	-	-	-	-	-	-	-	-	-	-	-	-	-
Ca-PT	-	-	-	-	-	-	-	-	-	-	-	-	-	-
La-PT	+	-	-	-	-	-	+	-	-	-	-	-	-	-
Nd-PT	+	-	-	-	-	-	-	-	-	-	-	-	-	-
Sm-PT	+	-	-	-	-	-	-	-	-	-	-	-	-	-
Gd-PT	+	-	-	-	-	-	-	-	-	-	-	-	-	-
PZT	-	-	-	-	-	-	+	-	-	-	-	-	-	-
PLZT	-	-	-	-	-	-	+	-	-	-	-	-	-	-
PMN	+	-	-	-	-	-	-	-	-	-	-	-	-	-
β-Sialon	+	-	-	-	-	-	-	-	-	-	-	-	-	-

* -, Incomplete or no dissolution of the sample; +, total dissolution of the sample.

of $(\text{NH}_4)_2\text{SO}_4 + \text{H}_2\text{SO}_4$, which has been used in open vessels (a beaker or platinum dish) with success in the literature, did not dissolve any of the sample. In all cases, the presence of HF was required. For the materials which contain lower levels of zirconium, such as PZT and PLZT, and also for the non-stabilized monoclinic zirconia ($m\text{-ZrO}_2$), the use of HCl with HF was sufficient to dissolve these samples. For the partially or fully stabilized zirconias, which are more refractory ceramics, the presence of stronger acids (HNO_3 or H_2SO_4) was required. It can be seen in Table 1 that the dissolution of such materials in PTFE bombs also required the presence of HF.

The materials with high levels of aluminium (Al_2O_3 , mullite and spinel), high levels of titanium (TiO_2 and BIT) or high levels of aluminium and titanium (Al_2TiO_5) also required the presence of HF, with HCl for materials with lower levels of these elements (mullite, spinel and BIT) or with H_2SO_4 or *aqua regia* for materials with high levels of those elements (Al_2O_3 , TiO_2 and Al_2TiO_5). In the dissolution procedures in PTFE bombs (Table 1), some workers also required the presence of HF to dissolve Al_2O_3 and mullite; however, other workers achieved the dissolution of these materials with HCl, H_2SO_4 or mixtures of $\text{HCl} + \text{H}_2\text{SO}_4$ or $\text{H}_2\text{SO}_4 + \text{HClO}_4$, by means of elevated temperatures ($> 200^\circ\text{C}$) and long times (even 24 h). For microwave-assisted dissolution, Tatár *et al.*⁴⁶ used only H_2SO_4 (1+1) to dissolve powders of alumina with different levels of the $\alpha\text{-Al}_2\text{O}_3$ phase, which is the crystalline phase of high temperature and with the highest chemical inertia. For the powders with high levels ($> 90\%$) of $\alpha\text{-Al}_2\text{O}_3$ dissolution times between 4 and 7 h are required. Matusiewicz³² used HCl and H_2SO_4 to dissolve in 20 min a commercial powder of Al_2O_3 .

To our knowledge, no procedure for dissolving $\text{CeO}_2\text{-Gd}_2\text{O}_3$ ceramics has been described previously. According to laboratory experience, alkali fusions were not fully efficient. However, complete dissolution was easily achieved by the microwave treatment with H_2SO_4 .

PMN, for which also no dissolution procedure has been described previously, was dissolved with HCl alone. BaTiO_3 was also dissolved by HCl treatment, which is the same acid used by others^{13,22,23,28} for dissolution in PTFE bombs (Table 1).

The use of HCl alone was sufficient to dissolve the rare earth element-modified lead titanates (La-PT, Nd-PT, Sm-PT and Gd-PT); however, Ca-PT required the additional use of HF.

The non-oxidic ceramics have shown varied behaviour. AlN has been dissolved with HCl alone, while other workers used HNO_3 ³² for microwave-assisted dissolution (Table 2) and HCl,^{12,30} HNO_3 ³² or *aqua regia*^{9,10} for acid decomposition in a PTFE bomb (Table 1). BN has been dissolved with HF and H_2O_2 , which are the same reagents as used by other workers to dissolve this material by acid decomposition in a PTFE bomb³² (Table 1) and by microwave-assisted digestion³² (Table 2). The dissolution of Si_3N_4 has been carried out with $\text{HCl} + \text{HF}$, which is the same acid mixture as used by Parker *et al.*³⁵ for acid decomposition in a PTFE bomb, whereas other workers required the use of $\text{HNO}_3 + \text{HF}$ ^{9,10,17,37,38} for acid decomposition in PTFE bomb or $\text{HF} + \text{H}_2\text{O}_2$ ³² for acid decomposition in a PTFE bomb or by microwave-assisted digestion.

SiC and β' -sialon are the only materials that could not be dissolved by means of any acid or mixture of acids tested. Also, no method for the microwave-assisted dissolution of these materials could be found in the literature. Only one method, used by Broekaert and co-workers in several studies,^{10,19,33,40} could be found for the acid decomposition of SiC powders with $\text{HNO}_3 + \text{H}_2\text{SO}_4 + \text{HF}$ in a PTFE bomb (Table 1). In fact, this is the main disadvantage of microwave-assisted dissolution, and in general of all acid decomposition

procedures, *i.e.*, not all the sintered advanced ceramics can be completely dissolved. In contrast, it can be stated, from our experience in the Chemical Analysis Department of the Institute of Ceramics and Glass, Madrid, Spain, that all sintered advanced ceramics can be dissolved by any fusion procedure, by using different types of crucibles, such as platinum, graphite, zirconium or nickel, and different types of fluxes, such as caustic alkalis (NaOH , KOH), Na_2O_2 , alkaline carbonates (Na_2CO_3 , K_2CO_3), boron compounds [$\text{Na}_2\text{B}_4\text{O}_7$, $\text{Li}_2\text{B}_4\text{O}_7$, LiBO_2 , $\text{Sr}(\text{BO}_2)_2$], Na_2CO_3 + a boron compound (B_2O_3 , H_3BO_3 , NaBO_2 , $\text{Na}_2\text{B}_4\text{O}_7$), Na_2CO_3 + a refractory oxide (usually ZnO), $\text{Na}_2\text{CO}_3 + \text{S}$, $\text{Na}_2\text{CO}_3 + \text{NaNO}_3$, KHSO_4 , alkali metal or ammonium fluorides (NH_4HF_2 , KHF_2 , NaF , KF , Na_2SiF_6 , NaBF_4 , $\text{H}_3\text{BO}_3 + \text{NaF}$, $\text{H}_3\text{BO}_3 + \text{LiF}$) or $\text{CaCO}_3 + \text{NH}_4\text{Cl}$. In this way, SiC can be dissolved by fusion with Na_2CO_3 in a platinum crucible and dissolution of the fused sample with hot water, and β' -sialon can be dissolved by fusion with $\text{Na}_2\text{CO}_3 + \text{Na}_2\text{B}_4\text{O}_7$ in a platinum crucible and dissolution of the fused sample with hot dilute HCl.

Table 7 shows 11 optimized methods which have been developed and which allow the microwave-assisted dissolution of all the advanced ceramic materials tested, except SiC and β' -sialon. All of them have a maximum of three stages, although several are developed in only two stages, and method 2 has only one stage. The microwave oven power used goes from 20% (120 W) to 60% (360 W), which is therefore much less than the maximum power of the equipment (600 W). The method times extend from 15 to 35 min, much shorter than that required to dissolve this type of material by acid decomposition in a PTFE bomb, as shown in Table 1.

As an example, Fig. 2 shows the results obtained in the analytical control by ICP-AES of BaTiO_3 attacked with 5 ml of HCl following microwave method 11. Solubilization of more than the 90% of the sample is achieved in the first 10–15 min, that is, in stage 1, and complete dissolution is achieved by increasing of the microwave oven power and by increasing the digestion time to 35 min. It can also be seen that the two elements are dissolved with different speeds. The element that requires more time for dissolution is Ti, because it has a higher refractoriness than Ba. This analytical control was carried out for all the materials, and all of them had a similar behaviour to BaTiO_3 , that is, most of the sample is solubilized in the first few minutes, usually at different speeds for each of the macro-constituents (the more refractory the element, the more slowly it is dissolved) and total dissolution is achieved by increasing of the microwave oven power and the digestion time.

Table 8 shows the complete procedures, that is, the acids or acid mixtures and the microwave method, which allow the dissolution of all the advanced ceramic materials studied (except SiC and β' -sialon, as mentioned previously). The most significant case is Al_2O_3 , which required three consecutive methods (methods 2, 3 and 1), each of them with different acids, to achieve its dissolution, because it is one of the most refractory ceramic materials that exists.

Fig. 3 shows the results obtained in the determination of some impurities in the attack reagents most frequently used in microwave-assisted dissolution, and in the attack reagents used in alkali fusions in graphite and platinum crucibles. The results corresponding to $\text{Li}_2\text{B}_4\text{O}_7$ alone (without HNO_3) are not included because this melting agent is not completely soluble in water. As can be seen, the level of impurities in the reagents used in the alkali fusions is higher than the amount of the impurities in the acids used in the microwave-assisted dissolution, in a ratio of 5–15 times for Ca, Fe, Si and Sr and nearly 100 times for Mg. This higher purity of the reagent blank solutions implies another great advantage of microwave-assisted dissolution over alkali fusions for the determination of elements at low concentrations in advanced ceramic materials. In addition, it must be remarked that, for all the attack

Table 7 Methods developed for the microwave-assisted dissolution of the advanced ceramic materials

Microwave method	Stage 1		Stage 2		Stage 3		Total time/min
	Time/min	Power/W	Time/min	Power/W	Time/min	Power/W	
1	15	180	10	240	10	180	35
2	15	120	—	—	—	—	15
3	15	150	10	180	—	—	25
4	15	180	5	240	10	180	30
5	15	180	5	240	—	—	20
6	10	120	5	180	5	120	20
7	15	180	5	300	—	—	20
8	10	180	5	240	5	120	20
9	15	240	10	300	—	—	25
10	10	240	10	300	5	360	25
11	15	180	10	300	10	180	35

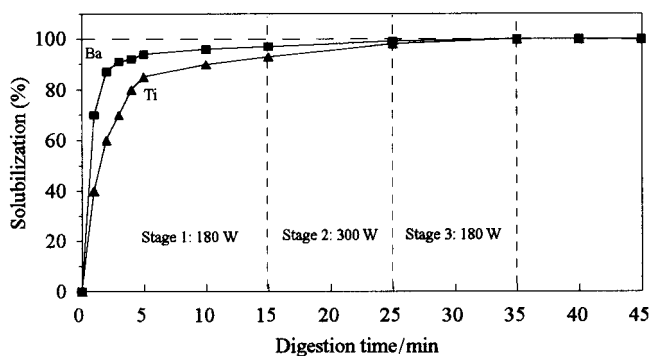


Fig. 2 Solubilization of BaTiO₃ ceramic material by microwave-assisted heating with 5 ml of HCl as a function of digestion time.

Table 8 Procedures for microwave-assisted dissolution of the advanced ceramic materials

Ceramic material (100 mg)	Acid or mixture of acids	Microwave method
m-ZrO ₂	5 ml HCl + 0.5 ml HF	1
Al ₂ O ₃	1.5 ml HF	2
	+ 3 ml HCl + 1 ml HNO ₃	3
	+ 2 ml HCl	1
TiO ₂	5 ml H ₂ SO ₄ + 1 ml HF	4
Ca-PSZ	5 ml HNO ₃ + 0.5 ml HF	5
Mg-PSZ	5 ml H ₂ SO ₄ + 0.5 ml HF	6
Y-FSZ	6 ml HNO ₃ + 1 ml HF	7
Ce-TZP	5 ml H ₂ SO ₄ + 0.5 ml HF	5
Yb-TZP	5 ml H ₂ SO ₄ + 0.5 ml HF	5
CeO ₂ -Gd ₂ O ₃	5 ml H ₂ SO ₄	8
Mullite	6 ml HCl + 1 ml HF	1
Spinel	6 ml HCl + 1 ml HF	1
Al ₂ TiO ₅	5 ml H ₂ SO ₄ + 0.5 ml HF	5
BIT	5 ml HCl + 0.5 ml HF	1
Y-TZP/Ce	5 ml H ₂ SO ₄ + 0.5 ml HF	5
AlN	5 ml HCl	5
BN	3 ml HF + 0.5 ml H ₂ O ₂	9
Si ₃ N ₄	3 ml HCl + 3 ml HF	10
SiC	—	—
BaTiO ₃	5 ml HCl	11
Ca-PT	5 ml HCl + 0.5 ml HF	1
La-PT	5 ml HCl	1
Nd-PT	5 ml HCl	1
Sm-PT	5 ml HCl	1
Gd-PT	6 ml HCl	1
PZT	5 ml HCl + 0.5 ml HF	1
PLZT	5 ml HCl + 0.5 ml HF	1
PMN	5 ml HCl	1
β'-Sialon	—	—

reagents, the amount of impurities found is lower than the limit guaranteed by the manufacturer (Merck).

Table 9 shows the results obtained in the determination of the detection limits of the minor elements in the matrix corresponding to hydrochloric acid microwave-assisted decomposition (5% HCl), in the matrix corresponding to alkali fusion in a graphite crucible (4% HNO₃ + 1% Li₂B₄O₇) and in the matrix corresponding to alkali fusion in a platinum crucible (10% HCl + 0.54% Na₂CO₃ + 0.46% Na₂B₄O₇). For comparison, the values reported by Boumans⁴⁸ are also shown. As can be seen, the detection limits obtained for all the elements, except Na and K, with microwave-assisted dissolution are lower than those achieved with alkali fusion. This may be due to the fact that the matrix effect in microwave digestion is lower because the reagent blanks (only acids) are the simplest, or because these reagent blanks have less impurities, as mentioned previously. For the alkali elements, the detection limits which are achieved with fusion are lower owing to the increase in the emission intensity that these elements undergo because of the effect of the decrease in ionization which takes place in the presence of large amounts of easily ionizable elements. Moreover, when the values obtained experimentally are compared with the detection limits reported by Boumans,⁴⁸ it can be noted that for all the elements, except Ca, Mg and Na, the experimental values are lower.

Tables 10 and 11 show the results obtained in the determi-

Table 9 Detection limits (ng ml⁻¹) obtained for some elements by ICP-AES in the dissolution of the advanced ceramic materials by acid microwave-assisted heating (matrix of 5% HCl) and by alkali fusion in a graphite crucible (matrix of 4% HNO₃ + 1% Li₂B₄O₇) and in a platinum crucible (matrix of 10% HCl + 0.54% Na₂CO₃ + 0.46% Na₂B₄O₇). For comparison, the detection limits reported by Boumans⁴⁸ are also given

Element	Microwave-assisted heating	Graphite crucible	Platinum crucible	Boumans ⁴⁸
Ca	0.17	0.22	0.24	0.13
Ce	4.69	5.24	5.58	32
Cu	1.47	1.73	1.87	3.6
Fe	2.10	2.38	2.51	3.4
Gd	8.72	9.25	11.7	13
K	188	154	146	—
La	0.79	0.88	0.91	6.7
Mg	0.16	0.19	0.20	0.1
Mn	0.18	0.22	0.22	0.93
Na	65	56	—	46
Nd	32.7	35.9	41.1	71
P	7.08	7.3	7.00	51
Si	2.71	2.92	3.32	8
Sm	4.13	4.62	4.87	36
Sr	0.024	0.026	0.027	0.28
Zr	0.11	0.13	0.13	4.7

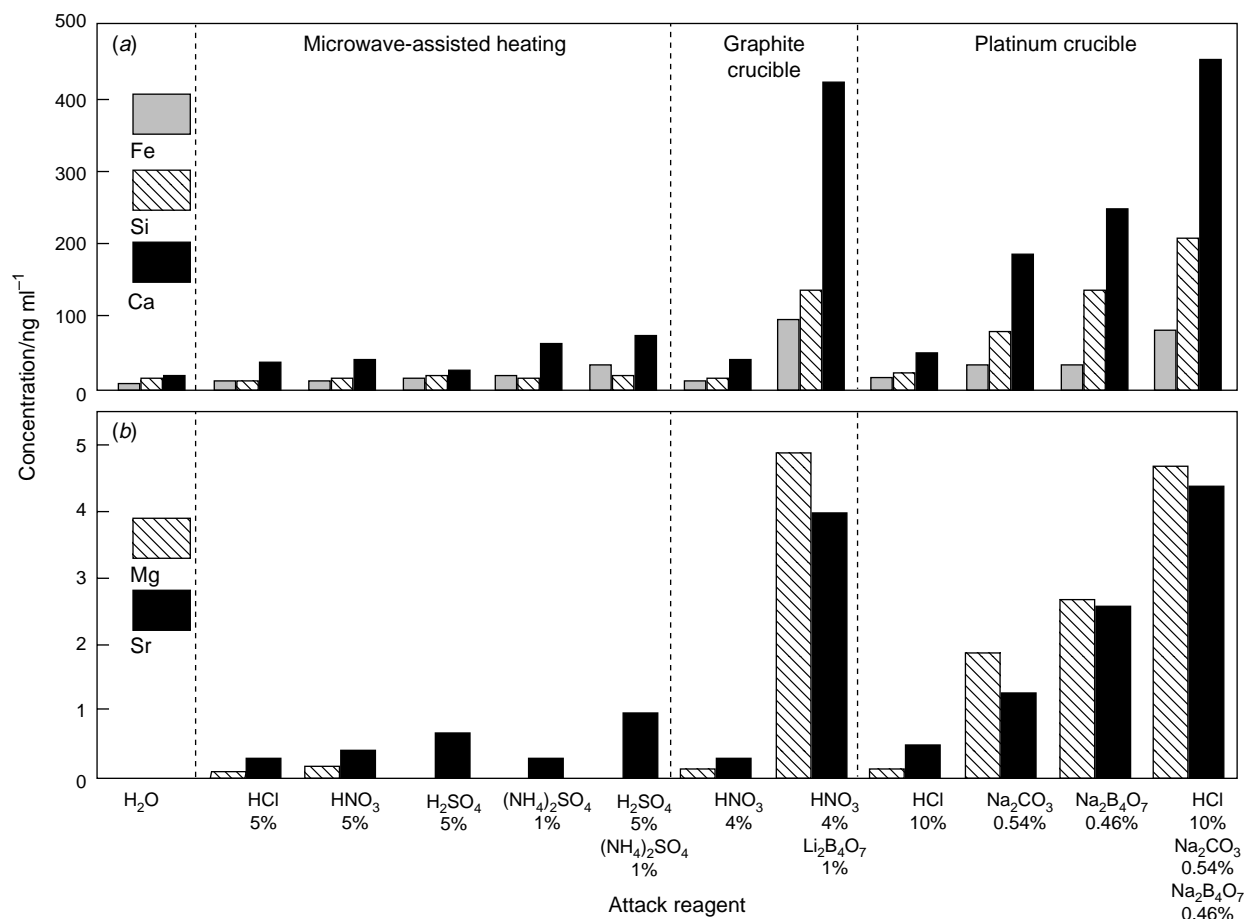


Fig. 3 Concentrations of (a) Fe, Si and Ca, and (b) Mg and Sr impurities found in some of the reagents used for the dissolution of the advanced ceramic materials by acid microwave-assisted heating and by alkali fusion with $\text{Li}_2\text{B}_4\text{O}_7$ in a graphite crucible and with $\text{Na}_2\text{CO}_3 + \text{Na}_2\text{B}_4\text{O}_7$ in a platinum crucible.

nation by ICP-AES of the macro-constituents and impurities, respectively, in the Gd-PT ceramic after dissolution by microwave heating with 6 ml of HCl following microwave method 1 (Table 8), by alkali fusion with $\text{Li}_2\text{B}_4\text{O}_7$ in a graphite crucible and by alkali fusion with $\text{Na}_2\text{CO}_3 + \text{Na}_2\text{B}_4\text{O}_7$ in a platinum crucible. For the macro-constituents (Table 10), the theoretical content of the three elements is also included for comparison. As can be seen, the results obtained for each element with the three dissolution methods are in good agreement. In the case of the macro-constituents they are also completely coincident with their theoretical contents. The RSD values which correspond to previous analytical results for the macro-constituents and the impurities are also given in Tables 10 and 11. As can be seen, for the macro-constituents the RSD values obtained are $<1\%$. For the impurities the RSD levels are generally between 1 and 10%. Higher values are only obtained for elements which are present at a very low concentration, such as K and Sr. A remarkable aspect is that, for all the elements the RSD values obtained in the chemical analysis of samples

dissolved by microwave-assisted digestion are much lower than those achieved by alkali fusion, *i.e.*, the precision obtained for the analytical results is much higher. Moreover, the determination of macro-constituents and impurities was also carried out on the other advanced ceramic materials and the results obtained (which are not included here for space reasons) are similar to those achieved for the Gd-PT ceramic. Hence it can be affirmed that the previous comments are applicable to all the advanced ceramic materials tested.

CONCLUSIONS

Sintered advanced ceramics are very refractory and chemically resistant materials. Their dissolution, consequently very difficult, is classically carried out with extreme chemical treatments (elevated temperature, long time and/or high concentration of reagents) by conventional acid decomposition and alkali fusion procedures. In this work, it has been demonstrated that these materials can be also dissolved by microwave-assisted heating.

Table 10 Analytical results obtained in the determination of macro-constituents by ICP-AES in the Gd-PT ceramic after dissolution by microwave-assisted heating with HCl and by alkali fusion with $\text{Li}_2\text{B}_4\text{O}_7$ in a graphite crucible and with $\text{Na}_2\text{CO}_3 + \text{Na}_2\text{B}_4\text{O}_7$ in a platinum crucible. For comparison, the theoretical composition of the sample is also given

Element	Microwave-assisted heating		Graphite crucible		Platinum crucible		Theoretical (%)
	Found (%)	RSD* (%)	Found (%)	RSD* (%)	Found (%)	RSD* (%)	
Gd	15.07	0.63	15.42	0.71	16.23	0.79	15.2
Pb	58.09	0.52	57.27	0.61	56.09	0.68	56.3
Ti	13.41	0.71	13.41	0.78	12.54	0.86	13.1

* $n=3$.

Table 11 Analytical results obtained in the determination of impurities by ICP-AES in the Gd-PT ceramic after dissolution by microwave-assisted heating with HCl and by alkali fusion with $\text{Li}_2\text{B}_4\text{O}_7$ in a graphite crucible and with $\text{Na}_2\text{CO}_3 + \text{Na}_2\text{B}_4\text{O}_7$ in a platinum crucible

Element	Microwave-assisted heating		Graphite crucible		Platinum crucible	
	Found (%)	RSD* (%)	Found (%)	RSD* (%)	Found (%)	RSD* (%)
Ca	108	4.6	114	7.9	117	12.8
Ce	420	1.4	427	2.1	418	2.9
Cu	110	5.4	112	8.9	114	10.5
Fe	122	4.9	131	8.4	126	6.3
K	58	8.6	53	15.1	61	16.4
La	90	3.3	94	5.3	87	6.9
Mg	432	2.5	428	3.3	435	2.8
Mn	3049	1.7	3038	2.7	3117	3
Na	214	5.6	207	10.6	—	—
Nd	192	3.1	203	5.4	200	4.5
P	248	3.2	250	4	244	3.7
Si	1450	2.1	1483	2.8	1462	2.6
Sm	215	3.2	220	5.4	204	7.3
Sr	9	11.1	8	25	10	20
Zr	258	3.1	261	3.8	255	5.5

* $n=3$.

Methods have been developed for the microwave-assisted dissolution of sintered bodies of a great variety of structural and electronic advanced ceramic materials. Evidently, these microwave methods are also applicable to the powders used as starting materials in the synthesis of such ceramics. These methods are simple (three stages maximum), fast (15–35 min digestion time) and mild (20–60% of the maximum microwave oven power).

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