

Description

This invention relates to the production of sintered glasses and ceramics; more particularly, it relates to the production of pure glass or ceramic products by vapour deposition and subsequent sintering.

The favoured commercial practice in the production of very pure glass products, such as glass optical waveguides, is by vapour deposition. The process conventionally involves the transport of vaporized reactants to an oxidation site, e.g. a burner or hot plasma zone, adjacent to a deposition substrate or within a glass deposition tube, oxidation of the reactants at the oxidation site to form a particulate oxide or soot oxidation product on the mandrel or tube and processing of the deposited soot to convert it to clear glass.

The vaporization characteristics of the reactants are critical for such processing. In commercial practice, these reactants have consisted of the volatile halides or hydrides of the selected metals or metalloids, e.g. the halides or oxyhalides of silicon, phosphorus, germanium and boron. These compounds have high vapour pressures at temperatures which are easy to maintain in a vapour delivery system and are converted to pure oxides at the oxidation site. In some cases, systems which operate at temperatures above the boiling temperature of the volatile halide or oxyhalide compound at atmospheric pressure have been used.

Suggestions have been made that other volatile compounds of these metals, such as the organometallic compounds, could be used, but there has been no commercial application of this proposal in the waveguide field. GB 2,071,644 suggests that silanes, chloro- and alkyl-substituted silanes and/or silicate esters may be used in vapour delivery systems for optical waveguide production, but, in general, the instability, high reactivity and/or limited vapour pressures of such compounds have mitigated against the use thereof.

It has been recognized that it would be desirable to use many of the common glass modifying oxides such as MgO , Na_2O , Al_2O_3 and CaO , in the fabrication of glass optical waveguide by vapour deposition techniques, but no satisfactory technique for incorporating these oxides in vapour-deposited glass has yet been developed. Most of the main group and rare earth metals useful as modifiers in transparent glasses do not form volatile chlorides or other volatile, but stable inorganic compounds. Thus, although they have potential utility as modifying dopants in glass waveguides, no successful technique for incorporating these oxides in vapour-deposited glass in high purity and with close control over concentration has been developed.

Proposals have been made to use metal alkyls as metal sources for the vapour deposition of oxides, but these compounds are generally so unstable as to be hazardous. For example, the compounds trimethyl-aluminium, $Al(CH_3)_3$, and dimethylzinc, $Zn(CH_3)_2$, are volatile and reactive, but are pyrophoric and thus very dangerous to store and to use.

U.S. Patent No. 3,801,294 discloses an early approach to the incorporation of main group modifiers in vapour-deposited oxide glasses wherein direct vaporization of metal halides from the solid state is proposed. This approach is disadvantageous because high delivery system temperatures must be maintained to achieve even moderate vapour pressures, and it is difficult to control the concentrations of dopants present in the carrier gas stream.

For example, M. Balog et al., in "Chemical Vapour Deposition and Characterization of HfO_2 Films from Organohafnium Compounds", *Thin Solid Films*, 41 (3) 247-259, describes the use of compounds such as $Hf(tfacac)_4$ and $Hf(thd)_4$ to form oxide films on heated surfaces by thermal deposition, but notes that the films tended to crack in thermal cycling if thick. EP—A—0055459 (Rikuun Electric) reports the use of $hfacac$ complexes in combination with H_2O vapour to form thin-film sensors, but there is no suggestion that such complexes could be used for the manufacture of bulk glass or ceramic products.

U.S. Patent No. 3,883,336 proposed an alternative approach for incorporating main group oxides in vapour-deposited glass wherein a solution containing a soluble salt of the desired metal is nebulized and the dispersed solution directed into an oxidation flame wherein metal oxide soot is generated. Unlike solvent-free vapour phase oxidation, this approach does not reproducibly provide an oxide soot having a particle size distribution such that it may be sintered into a void-free homogeneous mixed-oxide glass or ceramic. Moreover, the solvents used are potential sources of contamination in the product. Neither particulate oxide inclusions nor contaminating impurities may be tolerated in optical waveguide glass.

U.S. Patent Nos. 4,141,710 and 4,173,459 suggest an alternative technique for using solutions wherein a solvent carrying a thermally decomposable organic or inorganic compound of the desired metal is supplied to the inner surface of a bait tube or crucible. This process is one of thermal decomposition, rather than vapour phase oxidation, and is therefore not well suited to the fabrication of glass optical waveguides. The deposits produced by hot-surface thermal decomposition again differ significantly in morphology from the soots produced by vapour phase oxidation and often exhibit cracking and flaking if thick. Consequently, such deposits may be very difficult to convert to defect-free glass. Thus, while the thermal decomposition of inorganic and organometallic compounds, including metal chelates, such as the acetylacetonates, has been used to produce thin oxide films on glass sheet (G.B. 1,454,378 and G.B. 2,033,374A), and for metal plating (U.S. 3,356,527 and U.S. 3,049,797), such practices are not commercially adaptable to the fabrication of bulk glass products, such as optical waveguides.

It is therefore an object of the present invention to provide a process for the production of glass or other pure ceramic products which permits the incorporation of main group and rare earth metal oxides

into such products without undesirable voids or compositional discontinuities, such as particulate oxide inclusions.

It is a further object of the present invention to provide a process for fabricating glass optical waveguides incorporating such metal oxides as dopants wherein good control over the concentration of dopants in the vapour-deposited glass and high purity in the vapour deposition product may be achieved.

The present invention involves the use of selected vaporizable chelates of selected main group and rare earth metals as vapour sources for the production of pure glass and ceramic products by the consolidation of oxide soot produced by vapour phase oxidation. The process follows that presently used for the deposition of pure oxide glass-formers and glass-modifiers for products, such as optical waveguides, in that the metal compounds are vaporized and transported as vapour to an oxidation site where the compounds are reacted in the vapour phase to form finely divided soot. In current practice, this oxide soot is then captured and consolidated by heating to produce clear glass which may ultimately be formed into a product, such as an optical waveguide fibre. Such vapour deposition processes are advantageous because they permit the fabrication of very pure glass or ceramic products, i.e. products made of amorphous or crystalline materials incorporating not more than 0.01%, by weight, total of metallic impurities.

Thus, the present invention provides a process for the production of a glass or ceramic article by a vapour phase oxidation process wherein vapourized glass or ceramic source compounds are oxidized while in the vapour phase to form particulate oxide soot, the oxide soot is captured as deposited soot, and the deposited soot is sintered by heating to form a void-free, monolithic self-supporting glass or ceramic article, the article having a composition which includes at least one modifying oxide of a metal selected from Groups IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB and the rare earth series of the Periodic Table, characterized in that the vapourized source compound for at least one of the metal oxides of the article is a β -diketonate complex of the selected metal which exhibits a vapour pressure of at least 10 mm (Hg) (13.34 millibars) at a temperature not exceeding 250°C; and in that the vaporized β -diketonate complex is oxidized in the vapour phase to produce particulate oxide soot of the selected metal which is captured and sintered with the deposited soot.

Metals which may be transported in accordance with the present invention are selected from Groups IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB and the rare earth series of elements of the Periodic Table. These are provided as preparations of stable metal chelate compounds which may be vaporized at moderate temperatures and transported at substantial partial pressures. The transported chelate vapours are converted by vapour phase reaction at the reaction site to finely divide oxide soot having particle sizes and a particle size distribution suitable for capture and consolidation into a unitary or monolithic product, preferably a clear glass. The metal chelates used in the process are selected metal β -diketonates, i.e. complexes of the metal with one or more β -diketonate ligands derived from the class of diketones known as β -diketonates. The β -diketonate complex may include diketonate ligands only, or additional ligands may be present in the complex as adducts to the metal chelate structure.

Compounds selected from this group are liquids or solids at ambient temperatures and pressures. They are relatively stable against oxidation in air, yet may exhibit vapour pressures of over 10 mm Hg (13.34 millibars) and frequently over 100 mm Hg (133.4 millibars) at temperatures below the decomposition temperatures thereof. The selected compounds exhibit sufficient stability to be transported at these temperatures without significant decomposition, yet are readily reacted in the vapour phase to form pure metal oxides in the presence of oxygen at the reaction site, with or without additional heating depending upon the particular vapour phase reaction induced.

Utilizing these compounds, main group and rare earth elements may be transported in vapour form to a reaction site in substantial, but controllable concentrations without the use of a solvent carrier, so that high purity oxides of these metals in very finely-divided form suitable for sintering to clear glasses or fine-grained ceramics may be provided.

The present invention is illustrated by the accompanying drawings wherein:

Fig. 1 illustrates thermogravimetric curves for selected β -diketonate compounds suitable for use in accordance with the present invention;

Fig. 2 illustrates vapour pressure data for selected β -diketonate compounds suitable for use in accordance with the present invention;

Fig. 3 illustrates thermogravimetric curves showing the effects of adduct variation on the volatility of some adducted β -diketonate compounds; and

Fig. 4 illustrates an electron photomicrograph of a captured metal oxide soot provided in accordance with the present invention.

Oxides to be deposited by vapour phase oxidation in accordance with the present invention include the oxides of metals selected from Groups IA, IB, IIA, IIB, IIIA, IIIB, IVA and IVB of the Periodic Table. These may include oxides capable of forming glasses, e.g. aluminium oxide, but are predominantly oxides used as intermediates or modifiers in glass-forming systems, e.g. the alkali and alkaline earth metal oxides. Examples of candidate metals are as follows: Group IA — Li, Na; Group IB — Cu; Group IIA — Be, Mg; Group IIB — Zn, Cd, Hg; Group IIIB — Sc, Y; Group IIIA — Al, Ga; Group IVA — Sn; and Group IVB — Zr, Hf.

Rare earth metal oxides may also be deposited by vapour phase oxidation in accordance with the present invention. An example of a rare earth metal oxide which may be advantageously used as a dopant

in optical waveguide glass is CeO_2 , which in trace amounts may improve the resistance of waveguides to radiation damage. Other rare earth oxides which have been considered for use as glass modifiers in fused silica waveguides are La and Yb.

To be suitable for use in a vapour delivery system for vapour phase reaction, compounds of metals selected for incorporation in the deposited oxide must have a significant vapour pressure at some temperature below the compound's decomposition temperature. This vapour pressure requirement varies depending upon both the concentration of metal oxide needed in the deposition product and the deposition rate desired, but may range from as little as 1 mm Hg (1.334 millibars) for a compound needed in only trace amounts to a vapour pressure of at least 10 mm Hg (13.34 millibars), preferably at least 100 mm Hg (133.4 millibars) for compounds to be incorporated as major intermediate or glass-modifying constituents of the deposited glass.

The structure of the metal β -diketonate molecule is known to consist of a metal atom surrounded by β -diketone ligands corresponding to the general formula:

$[\text{R}-\text{CO}-\text{CH}(\text{CO}-\text{R}')^-]$. The R and R' constituents are typically alkyl or fluorinated alkyl groups containing from 1 to 4 carbon atoms. It is known that, for a given metal, the volatility of the corresponding metal β -diketonate depends strongly on the identity of the R and R' constituents.

Unsubstituted, low molecular weight diketones, such as acetylacetone (2,4-pentane-dione), have been used to form soluble metal complexes for the formation of metal oxide films by thermal decomposition on heated substrates. However, metal β -diketonates incorporating these ligands do not generally exhibit sufficient vapour pressures below the decomposition temperatures thereof to be useful vapour sources for the formation of main group metal oxides by vapour phase oxidation according to the present invention.

In contrast, metal β -diketonates wherein the β -diketone ligands are of higher formula weight (i.e. at least 153) and particularly wherein they are derived from fluorinated diketones, may exhibit significantly higher vapour pressures, and thus may be used to generate significant volumes of metal-containing vapours for the vapour phase generation of oxide soot. It has been theorized that the enhanced volatility of fluorine-substituted β -diketonate complexes is due to an effect on the van der Waals forces among chelate molecules caused by the high electronegativity of fluorine (R. E. Sievers, *et al.*, Science, 201, [4352], pp 217-223). For large fluorine-free ligands, steric hindrance may be a factor.

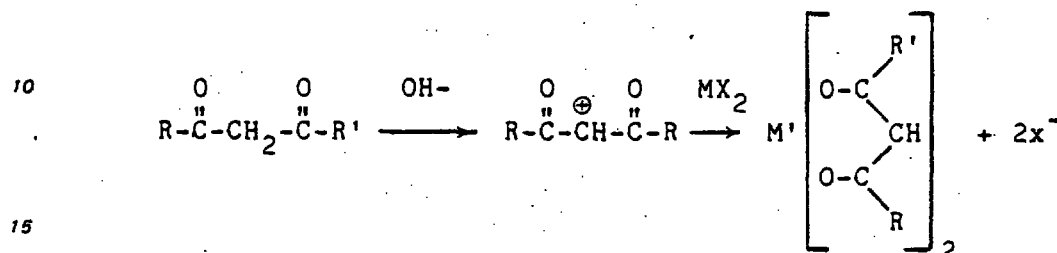
Examples of fluorinated and/or high molecular weight β -diketones suitable for complexing with main group or rare earth metals to form volatile metal chelates are reported in Table 1 below. Included in Table 1 for each named compound are a molecular structure for each compound, a symbol or trivial name used as a shorthand notation for the compound in subsequent Examples and boiling temperatures for each compound (reported at 760 mm Hg (1.01 bar), except where otherwise indicated). The H prefix in each of the shorthand notations (e.g. Hhfa) refers to the neutral compound in diketone form, while the diketonate anion form is written without the prefix, (hfa)⁻.

Table 1
Structures and Properties of β -diketones Used as Ligands

Compound	Structure	Trivial Name (Symbol)	Boiling Point
1,1,1-trifluoro-2,4-pentane-dione	$\begin{array}{c} \text{O} \\ \parallel \\ \text{F}_3\text{C}-\text{C}-\text{CH}_2-\text{C}-\text{CH}_3 \\ \parallel \\ \text{O} \end{array}$	trifluoroacetylacetone (Htfa)	B.P. = 107°C
1,1,1,5,5,5-hexafluoro-2,4-pentane-dione	$\begin{array}{c} \text{O} \\ \parallel \\ \text{F}_3\text{C}-\text{C}-\text{CH}_2-\text{C}-\text{CF}_3 \\ \parallel \\ \text{O} \end{array}$	hexafluoroacetylacetone (Hhfa)	B.P. = 70°C
2,2,6,6-tetramethyl-3,5-heptane-dione	$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ (\text{H}_3\text{C})_3\text{C}-\text{C}-\text{CH}_2-\text{C}-\text{C}(\text{CH}_3)_3 \\ \parallel \quad \parallel \\ \text{O} \quad \text{O} \end{array}$	(Hthd) or (Hdpm)	B.P. = 214-216°
6,6,7,7,8,8-heptafluoro-2,2-dimethyl-3,5-octane-dione	$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ (\text{H}_3\text{C})_3\text{C}-\text{C}-\text{CH}_2-\text{C}-(\text{CF}_2)_2-\text{CF}_3 \\ \parallel \quad \parallel \\ \text{O} \quad \text{O} \end{array}$	(Hfod)	B.P. = 33°
2,2,7-trimethyl-3,5-octane-dione	$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ (\text{H}_3\text{C})_3\text{C}-\text{C}-\text{CH}_2-\text{C}-\text{CH}_2-\text{CH}(\text{CH}_3)_2 \\ \parallel \quad \parallel \\ \text{O} \quad \text{O} \end{array}$	(Htod)	B.P. = 55°C (0.1 mm Hg/ 0.1334 mb)
1,1,1,5,5,6,6,7,7-decafluoro-2,7-heptane-dione	$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{F}_3\text{C}-\text{C}-\text{CH}_2-\text{C}-\text{CF}_2-\text{CF}_2-\text{CF}_3 \\ \parallel \quad \parallel \\ \text{O} \quad \text{O} \end{array}$	(Hdfhd)	B.P. = 99-105°C
1,1,1-trifluoro-6-methyl-2,4-heptane-dione	$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{F}_3\text{C}-\text{C}-\text{CH}_2-\text{C}-\text{CH}_2-\text{CH}(\text{CH}_3)_2 \\ \parallel \quad \parallel \\ \text{O} \quad \text{O} \end{array}$	(Htfmhd)	

Because of the practical requirement of high volatility, the use of the fluorinated β -diketonates of the main group and rare earth metals constitutes the preferred procedure for the vapour phase reaction of main group metals in accordance with the present invention and the use of one or more of the fluorinated ligands from Table 1 above is particularly preferred.

The mechanism of bonding in β -diketonate complexes is almost always through the oxygen atoms of the ligand, after deprotonation of the diketone to give the anion, as follows:



As is well known, the charge on the diketonate anion is actually delocalized about the $-\text{CO}-\text{CH}-\text{CO}-$ functional group, rather than at the central carbon atom as shown.

β -diketonate complexes usually exhibit high solubility in non-polar organic solvents, e.g. hexane or carbon tetra-chloride, with much lower solubility in alcohols or water. The production of these complexes has been described in the literature. See, for example, "Metal β -diketonates and Allied Derivatives", R. C. Mehrotra, R. Bohra and B. P. Gaur, Academic Press, New York, (1978).

Examples of specific β -diketonate complexes of metals which should exhibit vapour pressures of at least 10 mm Hg (13.34 millibars) without significant decomposition at temperatures of 250°C or below and thus should be suitable sources of those metals for reaction by vapour phase oxidation to provide metal oxides, are indicated in Table 2 below. Table 2 includes a listing of the metals as elements, together with an indication of which ligands are suitable for complexing therewith, the latter being identified by commonly used symbols as reported in Table 1 above.

Table 2
Volatile β -Diketonate Complexes

Elements	Ligands				
	(tfa) ⁻	(hfa) ⁻	(thd) ⁻	(dfhd) ⁻	(fod) ⁻
Li			X		
Na			X		
Be	X	X			
Mg		X		X	
Sc	X		X		
Y			X		X
Cu	X	X			X
Hf					X
Ti		X			
Zr		X			
Zn	X	X	X		
Cd		X			
Al	X	X			X
Ga	X	X			
Ce					X

Where only minor concentrations of a selected oxide are to be incorporated in a soot product, vapour pressures as high as 10 mm Hg (13.34 millibars) may not be required and pressures as low as 1 mm Hg (1.334 millibars) may provide sufficient metal vapour concentrations. An example of such a case is the incorporation of cerium oxide as a trace dopant to suppress radiation discolouration in a silicate core glass for an optical waveguide, where concentrations exceeding 0.1% CeO_2 , by weight, are rarely needed. $\text{Ce}(\text{tod})_4$ is an example of a rare earth metal β -diketonate which, while not demonstrating a vapour pressure

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as high as some of the above-described fluorinated β -diketonates exhibits sufficient vapour pressure to constitute a suitable vapour source for generating a small concentration of cerium oxide by vapour phase oxidation. Of course, even for trade doping, a more convenient practice would be to use a higher vapour pressure complex, such as $\text{Ce}(\text{fod})_4$, where such is available.

5 In many cases, β -diketonate complexes tend to form adducts with solvent molecules used in preparation, particularly when the complex is not coordinatively saturated and the solvent is a good Lewis base. The resulting adducted β -diketonate complexes may be quite stable and may themselves exhibit sufficient stability and volatility to constitute useful vapour sources. Examples of compounds which form adducts with β -diketonates are ammonia, water, pyridine, bipyridyl, phenanthroline, tetrahydrofuran and
10 dimethylformamide. These attach to the complex as additional ligands to achieve six-fold or higher coordination with the metal.

The method by which metal oxide soot is captured and consolidated to form a glass or other product, after being generated by the vapour phase oxidation of β -diketonate complexes in accordance with the present invention, is not critical. Prior art soot processing techniques may be used, including capturing the
15 soot on a suitable mandrel or bait rod, capturing the soot in a collection container, consolidating the captured soot by sintering on or off the bait or after shaping the loose soot by compaction or slip-casting and treating the captured soot prior to or during consolidation to remove non-metallic impurities, such as water, carbon or fluorine therefrom.

The following Examples describe β -diketonate compounds which have been prepared and, based on
20 the properties thereof, are considered suitable for use as main group metal sources for the production of pure oxides suitable for glass formation by vapour phase oxidation processes.

Example 1 — $\text{Al}(\text{hfa})_3$

A β -diketonate complex of aluminium (a Group IIIA metal) is prepared by reacting hexafluoroacetyl-
25 acetone (Hhfa) with aluminium chloride. A 1.06 g sample of AlCl_3 is added to 10 ml of CCl_4 with stirring under nitrogen. A solution of (Hhfa) in CCl_4 is slowly added to the AlCl_3 solution, with large amounts of HCl being evolved during the addition. The reaction mixture is refluxed for 30 minutes and the hot mixture is thereafter passed through a frit filter.

The clear filtrate crystallizes on cooling to give about 5.21 g of a white crystalline product. This product
30 is purified by vacuum sublimation at 80°C into a dry ice-cooled cold trap.

Infrared spectral analysis of a sample of the product in KBr corresponds to that reported in the literature for $\text{Al}(\text{hfa})_3$. This compound sublimes readily at temperatures above 50°C , melts at about $72\text{--}75^\circ\text{C}$ and has a reported vapour pressure of about 100 mm Hg (133.4 millibars) at 125°C . This indicates that the
35 compound would be a suitable source of aluminium-containing vapour for the production of sinterable oxide soot by a vapour phase reaction process.

Example 2 — $\text{Mg}(\text{hfa})_2$

β -diketonate complexes of the Group IIA metal magnesium are prepared by reacting (Hhfa) with basic
40 magnesium carbonate. A 2.5 g sample of basic magnesium carbonate, $\text{F MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ ($n = 6$), is suspended in 100 ml of ether with stirring under nitrogen. A 10.41 g sample of (Hhfa) is added to the suspension and the mixture is refluxed for 2 hours. The ether is then separated from a solid residual phase by decantation and evaporated to dryness. Evaporation leaves a residual white powder product identified as the ether-water adduct of magnesium hexafluoroacetylacetonate, $\text{Mg}(\text{hfa})_2 \cdot 1.5\text{Et}_2\text{O} \cdot \text{H}_2\text{O}$. This adducted complex melts at about 225°C and may be vaporized by sublimation at 165°C .

45 To prepare a tetrahydrofuran (THF) adduct of $\text{Mg}(\text{hfa})_2$, a 20 ml volume of THF is added to the ether-water adduct produced as described above and the resulting solution is stirred for 18 hours. Rotary evaporation of the solution leaves a white powder residue identified by proton nuclear magnetic resonance (nmr) as $\text{Mg}(\text{hfa})_2 \cdot 4\text{THF}$. Sublimation of this compound to a dry ice-cooled cold trap produces the adduct $\text{Mg}(\text{hfa})_2 \cdot 2\text{THF}$, a compound having a melting point of approximately 130°C which may be vaporized at
50 160°C to generate Mg-containing vapours for a vapour phase oxidation process.

Example 3 — $\text{Na}(\text{tfmhd})$

A β -diketonate complex of the Group IA metal sodium is prepared by reacting sodium hydroxide with a
55 beta-diketone containing a 7-carbon chain. A 4.08 g sample of pelletized NaOH is dissolved in 50 ml of water in a separatory funnel and 20.0 g of the diketone 1,1,1-trifluoro-6-methyl-2,4-heptane-dione (Htfmhd) is added to the solution. This mixture is shaken periodically over a 15-minute interval and then ether is added to extract the Na- β -diketonate product from the mixture. The pale yellow ether extract is evaporated to dryness in air giving a pale yellow solid identified as $\text{Na}(\text{tfmhd})$, having an undetermined melting point, but giving evidence of sublimation at about 260°C with some evidence of thermal decomposition.

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Example 4 — $\text{Ce}(\text{fod})_4$

A β -diketonate complex of the rare earth metal cerium prepared by reacting cerium nitrate with 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione.

65 A 68.2 g sample of this β -diketone (Hfod) is added to 115 ml of 2M aqueous NH_4OH , resulting in a white precipitate which is separated and dissolved in 200 ml of water and 200 ml of methanol. The resulting

solution is placed in an addition funnel and added dropwise to a nitric acid solution of cerium nitrate consisting of 25.0 g $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ dissolved in 60 ml of 1.4 M HNO_3 . 2M NH_4OH is then added to achieve and maintain pH 6.

The resulting mixture separates into a red oil phase and an aqueous phase. The separate mixture is stirred under O_2 at room temperature until oxidation of Ce^{3+} to Ce^{4+} is complete, in this case about 70 hours. Thereafter, 200 ml of hexanes are added and the organic layer containing the product is separated from the aqueous phase, filtered and evaporated to dryness in a rotary evaporator. The product is crystallized from the red oil and examination of the proton nmr spectrum of the crystals shows substantially complete oxidation to $\text{Ce}(\text{fod})_4$.

After purification by sublimation, the thus-produced $\text{Ce}(\text{fod})_4$ exhibits a melting point of about 97°C and a vapour pressure approaching 10 mm Hg (13.34 millibars) at a temperature near 200°C . By virtue of this high vapour pressure, this compound would constitute a suitable source of Ce-containing vapours for a vapour phase oxidation process in accordance with the present invention.

Example 5 — $\text{Zn}(\text{hfa})_2 \cdot 1.5 \text{ THF}$

Following the procedure reported by Chatteraj, *et al.*, J. Inorg. Nucl. Chem., 28, (1966), pages 1937-1943, the water adduct of $\text{Zn}(\text{hfa})_2$ is prepared by reacting Hhfa with zinc oxide. 10 grams of ZnO and 35.2 ml of Hhfa are added to a flask equipped with a condenser, magnetic stirrer and heating mantle, with stirring to disperse the ZnO . 30 ml of H_2O is added, causing the reflux of Hhfa due to the evolution of heat, with stirring being continued until all evidence of reaction has ceased.

An additional 30 ml of water and 200 ml of ether are then added and the mixture is refluxed for 1 hour. After cooling, excess ZnO is removed by filtration, the ether layer is separated and dried by adding $4\text{\AA}$ ($4 \times 10^{-12}\text{m}$) molecular sieves, filtered and the ether is then evaporated to give 55 g of crude $\text{Zn}(\text{hfa})_2 \cdot 2\text{H}_2\text{O}$ product.

Approximately 10 g of this product is dissolved in THF at room temperature, the solvent is then evaporated and the residue is sublimed at 150°C under vacuum to a dry ice-cooled cold trap. Infra-red spectra, nuclear magnetic resonance, thermogravimetric analysis, elemental analysis and differential scanning calorimetry are used to characterize this compound. The compound is presently believed to have the chemical formula $\text{Zn}(\text{hfa})_2 \cdot 2\text{THF}$, with a melting temperature of 165°C . It exhibits excellent thermal stability, showing only slight decomposition when maintained at 165°C for about 60 hours.

Figure 1 of the accompanying drawings illustrates the vaporization characteristics for selected β -diketonate complexes such as reported in the above Examples, as determined by thermogravimetric analysis. The drawing plots weight loss of a sample of the complex as a function of temperature over the heating range from 25 - 500°C . Temperature is plotted on the horizontal axis with the vertical axis corresponding to relative weight loss in the sample.

In general, easy vaporization without decomposition is reflected by an analysis trace exhibiting a sharp vertical drop corresponding to rapid weight loss of the heated sample in the evaporation or sublimation range, followed by a sharp horizontal trace as higher temperatures evidencing the absence of decomposable residues. The most desirable vaporization characteristics are demonstrated by $\text{Al}(\text{hfa})_3$, $\text{Zn}(\text{hfa})_2 \cdot 2\text{THF}$ and $\text{Mg}(\text{hfa})_2 \cdot 2\text{THF}$, which exhibit rapid and complete vaporization at temperatures in the 100 - 200°C range. This may be contrasted with the behaviour of a complex, such as $\text{Mg}(\text{hfa})_2 \cdot \text{PCl}_3$, an adducted complex hereinafter described with reference to accompanying Fig. 3, which exhibits evidence of significant decomposition and incomplete volatilization even at temperatures in excess of 300°C .

Fig. 2 of the accompanying drawings illustrates vapour pressure as a function of temperature for the $\text{Al}(\text{hfa})_3$ and $\text{Mg}(\text{hfa})_2 \cdot 2\text{THF}$ β -diketonate complexes. This plot shows the very substantial vapour pressures of these two complexes, which are in the range of at least 10-100 mm Hg (13.34-133.4 millibars) at temperatures in the range of 100 - 200°C .

Significant variations in volatility may occur when β -diketonate compounds, such as described above, are complexed with Lewis bases to form adducted metal β -diketonates. To demonstrate some of these variations, adducts of $\text{Mg}(\text{hfa})_2$ with five different Lewis bases were prepared by adding small quantities of the sublimed ether-water adduct $\text{Mf}(\text{hfa})_2 \cdot 1.5\text{Et}_2\text{O} \cdot \text{H}_2\text{O}$ to diethyl ether solutions of each of the six adducts: pyridine, CH_3CN , PCl_3 , dioxane and dimethyl formamide (DMF), with overnight stirring, followed by evaporation to dryness and sublimation under vacuum to obtain the products. The volatility of each of the adducts is then evaluated by thermogravimetric analysis.

Fig. 3 of the accompanying drawings illustrates thermogravimetric curves for the five different adducts $\text{Mg}(\text{hfa})_2 \cdot x\text{L}$ wherein L represents pyridine ($\text{C}_5\text{H}_5\text{N}$), CH_3CN , PCl_3 , dioxane ($\text{C}_4\text{H}_8\text{O}_2$) or DMF ($(\text{CH}_3)_2\text{NCOH}$) as indicated in the drawing. The proportions x of these ligands L in the adduct molecules were not determined. A curve for $\text{Mg}(\text{hfa})_2 \cdot 2\text{THF}$ is also included for comparison. The CH_3CN and PCl_3 adducts show evidence of decomposition, while the other adducts evaporate completely within narrow ranges of temperature, but at vaporization temperatures which vary significantly depending upon the identity of the particular adduct employed. $\text{Mg}(\text{hfa})_2 \cdot 2\text{THF}$ is found to be the most volatile of the various adducts tested.

The requirement that the metal compound be sufficiently volatile for efficient vaporization and vapour phase transport in accordance with the present invention arises because of the need to generate a soot product having a relatively small particle size. For example, to obtain void-free glasses by the viscous sintering of oxide soot, particle sizes not exceeding 0.1 microns (10^{-7}m) are normally preferred. The

following Examples demonstrate the utility of selected volatile β -diketonate compounds for the production by vapour phase oxidation of fine, homogeneous oxide soot.

Example 6 — $\gamma\text{Al}_2\text{O}_3$

A quantity of $\text{Al}(\text{hfa})_3$ produced as in Example 1 above is maintained in a liquid state in a glass container by heating to about 125°C . A helium carrier gas is bubbled through the liquid $\text{Al}(\text{hfa})_3$ (the latter having a vapour pressure of about 100 mm Hg (133.4 millibar) at this temperature) and the He carrier then transports vaporized $\text{Al}(\text{hfa})_3$ out of the container to an operating flame-oxidation burner through a heated delivery line. The flame oxidation burner is of the type described in U.S. Patent No. 4,125,288, having a design permitting the introduction of a vapour reactant stream into the burner flame via a centre orifice in the burner face.

The $\text{Al}(\text{hfa})_3$ is oxidized in the vapour phase in the methane-oxygen burner flame to produce a $\gamma\text{-Al}_2\text{O}_3$ soot which is collected for examination. Fig. 4 of the accompanying drawings illustrates an electron photomicrograph for a sample of the $\gamma\text{-Al}_2\text{O}_3$ soot thus provided, wherein the bar corresponds to a dimension of 0.1 microns (10^{-7}m).

As is evident from the study of accompanying Fig. 4, the $\gamma\text{-Al}_2\text{O}_3$ soot produced by $\text{Al}(\text{hfa})_3$ oxidation in accordance with the present invention is in the form of very small (<0.1 microns/ 10^{-7}m) spherical particles, the bulk of which ranges from 0.025 to 0.05 microns ($\times 10^{-6}\text{m}$) in size. This indicates that the material could readily be incorporated into ceramics or void-free glasses of a desired composition by a sintering consolidation process.

Example 7 — MgO-SiO_2 Glass

A quantity of $\text{Mg}(\text{hfa})_2 \cdot 2\text{THF}$ produced as described in Example 3 above is maintained in a liquid state in a glass container by heating to about 190°C , a temperature at which it has a vapour pressure of about 500 mm Hg (667 mb). An argon carrier gas is bubbled through this liquid at a rate of about 72 cc/min and vaporized $\text{Mg}(\text{hfa})_2 \cdot 2\text{THF}$ is transported by this carrier through a heated delivery line to an operating methane-oxygen burner of the type used in Example 6 above.

A second reactant stream, transported by a second delivery line and combined with the $\text{Mg}(\text{hfa})_2 \cdot 2\text{THF}$ -carrying stream at the burner, is produced by bubbling argon at a rate of 576 cc/min through a quantity of SiCl_4 maintained at 35°C , a temperature at which SiCl_4 has a vapour pressure of 530 mm Hg (707 mb). The combined reactant stream is fed into the burner flame, that flame resulting from the combustion of 3.5 l/min of natural gas (methane) and 3.4 l/min of oxygen.

The SiCl_4 and $\text{Mg}(\text{hfa})_2 \cdot 2\text{THF}$ reactants are converted by vapour phase oxidation in the flame to SiO_2 and MgO , each in the form of a finely divided oxide soot. This soot mixture is collected on an alumina mandrel for examination, analysis and further treatment.

Analysis of the collected soot determines that a soot mixture consisting of 1.21% MgO and the remainder SiO_2 has been deposited on the mandrel. This soot mixture is consolidated by heating with a gas-oxygen flame to sinter the soot into a clear MgO-SiO_2 glass having a refractive index of about 1.460.

Example 8 — MgO-SiO_2 Opal Glass

The glass-forming procedure of Example 7 is repeated, except that argon carrier gas flow through the liquid $\text{Mg}(\text{hfa})_2 \cdot 2\text{THF}$ reactant is increased to 720 cc/min, such that the soot mixture collected from the vapour phase oxidation of the reactant stream contains 7.74% MgO and the remainder SiO_2 by weight. This soot mixture is sintered in a gas-oxygen flame as in Example 6 and the product is a dense, substantially void free MgO-SiO_2 opal glass.

In using β -diketonate complexes as sources of main group metals for vapour phase oxidation processes, it must be recognized that these complexes may undergo reaction at vapour delivery temperatures which may adversely affect the desirable vaporization and stability characteristics thereof. Reactions to be considered which might reduce the volatility of the complex include electrophilic substitution of a halogen for a hydrogen atom on the β -diketone ligand, adduct formation by the complexing of the β -diketonate molecule with selected bases, replacement reactions wherein a β -diketonate ligand is replaced by a halide and redistribution reactions wherein ligands are scrambled among various metal complexes to produce new complexes of low volatility. Avoidance of these reactions may require the use of delivery systems wherein each vaporized reactant is separately transported to the reaction site for final mixing and vapour phase oxidation.

While the foregoing description has been primarily concerned with processes suitable for the formation of optically clear glasses useful, for example, in the fabrication of glass optical waveguides, it will be appreciated that the present invention is applicable to the production of other pure unitary ceramic products, such as opal glass, semi-crystalline glasses, or crystalline ceramics, including porous glasses or ceramics where only partial sintering of the oxide soot is permitted in the consolidation step. In addition, it is possible to process the oxide soot prior to consolidation if, for example, it is desired to shape the soot into a preform of a desired configuration. This may be done, for example, by dispersing the soot in a suitable vehicle and casting the dispersion into a selected shape.

Claims

1. A process for the production of a glass or ceramic article by a vapour phase oxidation process wherein vapourized glass or ceramic source compounds are oxidized while in the vapour phase to form particulate oxide soot, the oxide soot is captured as deposited soot, and the deposited soot is sintered by heating to form a void-free, monolithic self-supporting glass or ceramic article, the article having a composition which includes at least one modifying oxide of a metal selected from Groups IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB and the rare earth series of the Periodic Table, characterized in that the vapourized source compound for at least one of the metal oxides of the article is a β -diketonate complex of the selected metal which exhibits a vapour pressure of at least 10 mm (Hg) (13.34 millibars) at a temperature not exceeding 250°C; and in that the vapourized β -diketonate complex is oxidized in the vapour phase to produce particulate oxide soot of the selected metal which is captured and sintered with the deposited soot.
2. A process for the production of a glass optical waveguide comprising a vapour phase oxidation process wherein vapourized compounds of glass or ceramic source compounds are oxidized while in the vapour phase to form particulate oxide soot, the glass having a composition which includes at least one modifying oxide of a metal selected from Groups IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB and the rare earth series of the Periodic Table, wherein the soot is captured and consolidated into clear glass and the glass is drawn into optical waveguide fibre, characterised in that the vapourized source compound for at least one of the metal oxides of the article is a β -diketonate complex of the selected metal which exhibits a vapour pressure of at least 10 mm (Hg) (13.34 millibars) at a temperature not exceeding 250°C; and in that the vapourized β -diketonate complex is oxidized in the vapour phase to produce particulate oxide soot of the selected metal which is captured and sintered with the deposited soot.
3. A process as claimed in claim 1 or claim 2, wherein the metal is selected from Li, Na, Be, Mg, Sc, Y, Cu, Hf, Zr, Ti, Zn, Cd, Al, Ga, Tl and Ce.
4. A process as claimed in any of claims 1 to 3 wherein the β -diketonate complex comprises a β -diketonate ligand having a formula weight of at least 153.
5. A process as claimed in any of claims 1 to 4 wherein the β -diketonate ligand is derived from a fluorinated β -diketone.
6. A process as claimed in any of claims 1 to 4 wherein the β -diketonate ligand is selected from (tfa), (hfa), (thd), (dfhd), (tod) and (fod) ligands.
7. A process as claimed in any of claims 1 to 6 wherein the β -diketonate complex is adducted with at least one Lewis base.
8. A process as claimed in claim 7 wherein the Lewis base is tetrahydrofuran.
9. A process as claimed in any of claims 1 to 8 wherein the particulate metal oxide soot is captured on a rotating mandrel.
10. A process as claimed in any of claims 1 to 9 wherein the captured soot is treated prior to or during consolidation to remove water, carbon and/or fluorine impurities therefrom.

40 Patentansprüche

1. Verfahren zur Herstellung eines Glas- oder Keramikartikels durch einen Dampfphasenoxidationsprozeß, wobei verdampfte Glas- oder Keramik-Ausgangs-Verbindungen oxidiert werden, während sie sich in der Dampfphase befinden, um einen aus Oxidpartikeln bestehenden Ruß zu bilden, der als abgeschiedener Ruß eingefangen und durch Erhitzen gesintert wird, um einen von Gasblasen freien, monolithischen selbsttragenden Glas- oder Keramikartikel zu formen, wobei der Artikel eine Zusammensetzung hat, die wenigstens ein modifizierendes Metalloxid, ausgewählt aus den Gruppen IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB und den seltenen Erden des Periodensystems, einschließt, dadurch gekennzeichnet, daß die verdampfte Ausgangs-Verbindung für wenigstens eines der Metalloxide des Artikels ein β -Diketonat-Komplex des ausgewählten Metalls ist, der einen Dampfdruck von wenigstens 10 mm (Hg) (13.34 Millibar) bei einer Temperatur von nicht über 250°C aufweist und daß der verdampfte β -Diketonat-Komplex in der Dampfphase oxidiert wird, um einen aus Oxidpartikeln bestehenden Ruß des ausgewählten Metalls zu ergeben, der eingefangen und mit dem abgeschiedenen Ruß gesintert wird.
2. Verfahren zur Herstellung eines Lichtwellenleiters umfassend einen Dampfphasenoxidationsprozeß, wobei verdampfte Verbindungen von Glas- oder Keramik-Ausgangs-Verbindungen oxidiert werden, während sie sich in der Dampfphase befinden, um einen aus Partikeln bestehenden Oxidruß zu bilden, und das Glas aus einer Zusammensetzung besteht, die wenigstens ein modifizierendes Metalloxid einschließt, welches aus den Gruppen IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB und den seltenen Erden des Periodensystems ausgewählt wurde, wobei der Ruß eingefangen und zu klarem Glas konsolidiert und das Glas zu einer Lichtwellenleiter-Faser gezogen wird, dadurch gekennzeichnet, daß die verdampfte Ausgangs-Verbindung für wenigstens eines der Metalloxide des Artikels ein β -Diketonat-Komplex des ausgewählten Metalls ist, der einen Dampfdruck von wenigstens 10 mm (Hg) (13.34 Millibar) bei einer Temperatur von nicht über 250°C aufweist und daß der verdampfte β -Diketonat-Komplex in der Dampfphase oxidiert wird, um einen aus Oxidpartikeln bestehenden Ruß des ausgewählten Metalls zu ergeben, der eingefangen und mit dem abgeschiedenen Ruß gesintert wird.



3. Verfahren nach Anspruch 1 oder 2, wobei das Metall aus Li, Na, Be, Mg, Sc, Y, Cu, Hf, Zr, Ti, Zn, Cd, Al, Ga, Tl und Ce ausgewählt wird.

4. Verfahren nach einem der Ansprüche 1 bis 3, wobei der β -Diketonat-Komplex einen β -Diketonatliganden mit einem Formelgewicht von wenigstens 153 umfaßt.

5. Verfahren nach einem der Ansprüche 1 bis 4, wobei der β -Diketonatligand von einem fluorierten β -Diketon abgeleitet wird.

6. Verfahren nach einem der Ansprüche 1 bis 4, wobei der β -Diketonatligand ausgewählt wird aus (tfa), (hfa), (thd), (dfhd), (tod) und (fod) Liganden.

7. Verfahren nach einem der Ansprüche 1 bis 6, wobei der β -Diketonat-Komplex ein Addukt mit wenigstens einer Lewis-Base ist.

8. Verfahren nach Anspruch 7, wobei die Lewis-Base Tetrahydrofuran ist.

9. Verfahren nach einem der Ansprüche 1 bis 8, wobei der aus Metalloxidpartikeln bestehende Ruß auf einem rotierenden Dorn eingefangen wird.

10. Verfahren nach einem der Ansprüche 1 bis 9, wobei der eingefangene Ruß vor oder während der Konsolidierung behandelt wird, um Wasser, Kohlenstoff- und/oder Fluorverunreinigungen daraus zu entfernen.

Revendications

1. Un procédé pour la production d'un article en verre ou matière céramique par un procédé d'oxydation en phase vapeur dans lequel des composés-sources de verre ou de matière céramique vaporisés sont oxydés tandis qu'ils se trouvent en phase vapeur pour former une suie d'oxydes particuliers, la suie d'oxydes est collectée sous forme de suie déposée, et la suie déposée est frittée par chauffage pour former un article monolithique, sans vides, auto-portant, en verre ou matière céramique, l'article ayant une composition qui inclut au moins un oxyde modificateur d'un métal choisi dans les Groupes IA, IB, IIA, IIB, IIIA, IIIB, IVA et IVB et la série des terres rares du tableau périodique, caractérisé en ce que le composé-source vaporisé correspondant à l'un au moins des oxydes de métaux de l'article est un complexe β -dicétonate du métal choisi, qui présente une pression de vapeur d'au moins 10 mm (Hg) (13,34 millibars) à une température ne dépassant pas 250°C; et en ce que le complexe β -dicétonate vaporisé est oxydé en phase vapeur pour produire une suie d'oxyde particulaire du métal choisi qui est collectée et frittée avec la suie déposée.

2. Un procédé pour la production d'un guide d'onde optique en verre comprenant un procédé d'oxydation en phase vapeur dans lequel des composés-sources de verre ou de matière céramique vaporisés sont oxydés tandis qu'ils se trouvent en phase vapeur pour former une suie d'oxydes particuliers, le verre ayant une composition qui inclut au moins un oxyde modificateur d'un métal choisi dans les Groupes IA, IB, IIA, IIB, IIIA, IIIB, IVA et IVB et la série des terres rares du tableau périodique, dans lequel la suie est collectée et consolidée en un verre transparent et le verre est étiré pour former une fibre optique guide d'onde, caractérisé en ce que le composé-source vaporisé correspondant à l'un au moins des oxydes de métaux de l'article est un complexe β -dicétonate du métal choisi, qui présente une pression de vapeur d'au moins 10 mm (Hg) (13,34 millibars) à une température ne dépassant pas 250°C; et en ce que le complexe β -dicétonate vaporisé est oxydé en phase vapeur pour produire une suie d'oxyde particulaire du métal choisi qui est collectée et frittée avec la suie déposée.

3. Un procédé tel que revendiqué dans la revendication 1 ou la revendication 2, dans lequel le métal est choisi parmi Li, Na, Be, Mg, Sc, Y, Cu, Hf, Zr, Ti, Zn, Cd, Al, Ga, Tl et Ce.

4. Un procédé tel que revendiqué dans l'une quelconque des revendications 1 à 3, dans lequel le complexe β -dicétonate comprend un ligand β -dicétonate ayant un poids de formule d'au moins 153.

5. Un procédé tel que revendiqué dans l'une quelconque des revendications 1 à 4, dans lequel le ligand β -dicétonate est dérivé d'une β -dicétone fluorée.

6. Un procédé tel que revendiqué dans l'une quelconque des revendications 1 à 4, dans lequel le ligand β -dicétonate est choisi parmi les ligands (tfa), (hfa), (thd), (dfhd), (tod) et (fod).

7. Un procédé tel que revendiqué dans l'une quelconque des revendications 1 à 6, dans lequel le complexe β -dicétonate est sous forme d'un produit d'addition avec au moins une base de Lewis.

8. Un procédé tel que revendiqué dans la revendication 7, dans lequel la base de Lewis est le tétrahydrofuranne.

9. Un procédé tel que revendiqué dans l'une quelconque des revendications 1 à 8, dans lequel la suie d'oxydes de métaux particuliers est collectée sur un mandrin rotatif.

10. Un procédé tel que revendiqué dans l'une quelconque des revendications 1 à 9, dans lequel la suie collectée est traitée avant ou pendant la consolidation pour en éliminer l'eau, le carbone et/ou le fluor présents comme impuretés.



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