Synthesis and Characterization of Monosized Doped TiO₂ Powders

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Monosized spheroidal doped TiO₂ particles with an average diameter of 0.3 to 0.7 μm were prepared by the controlled cohydrolysis of mixtures of titanium alkoxide and either niobium or tantalum alkoxide. An inorganic salt precipitation technique was used to put Ba, Cu, or Sr onto the surface of singly doped TiO₂ particles. Chemical analyses by several methods demonstrated the reproducibility and reliability of the doping procedures.

RECENTLY, Barringer and Bowen[1] described the synthesis of monosized, pure TiO₂ powders by the controlled hydrolysis of alcoholic solutions of titanium alkoxides. The present communication describes the synthesis, physical characterization, and chemical characterization of monosized doped TiO₂ powders made by the controlled hydrolysis of mixtures of metal alkoxides and by inorganic salt precipitation reactions. These powders are doped with pentavalent cations such as Nb^{5+} or Ta^{5+} and may also be doped with divalent cations such as Ba^{2+}, Cu^{2+}, or Sr^{2+}. The techniques described, which are analogous to inorganic salt coprecipitation techniques described previously,[2] are easily applied to other systems and have been used to prepare other oxide powders (e.g. ZrO_2, Y_2O_3-doped ZrO_2, ZnO, doped-ZnO) of controlled size, shape, and composition.[3]

The TiO₂ ceramics doped with various combinations of the cations listed previously have been studied for use as low-voltage varistors and are under study as grain-boundary capacitor materials.[4] Donor-doped, conductive TiO₂ ceramics have also been used as oxygen sensors[5] and current-collecting electrodes in Na-S batteries.[6] These ceramics are prepared by conventional processing methods such as ball-milling oxides (or other precursors) or by drying slurries of powder in liquid containing the desired cation dopants.[6,7] Often, however, these methods do not yield a homogeneously doped ceramic.[6] The techniques described in this communication are advantageous over the conventional techniques because they yield oxides that are homogeneously doped on a microscopic (≤0.1 μm) scale. Furthermore, they yield oxide powders of controlled size and shape which can be packed easily into controlled structures.[1,3] (Packing and sintering of the monosized, doped TiO₂ particles will be described elsewhere.) Finally, if desired, particles with controlled chemical heterogeneity, e.g. an onion skin-like structure, can also be prepared by these doping techniques.

EXPERIMENTAL PROCEDURE

Several different doped TiO₂ powders[8] were prepared by the controlled hydrolysis of titanium tetraethoxide, $Ti(OC_2H_5)_4$,* or titanium tetraisopropoxide, $Ti(^iOC_3H_7)_4$.* Most of the results presented are for the doped TiO₂ powders made from the titanium tetraethoxide; however, the synthesis procedures and many of the results also apply to doped TiO₂ powders made from the titanium tetraisopropoxide.

The TiO₂ powders doped with either Ta₂O₅ or Nb₂O₅ were made by the controlled cohydrolysis of dilute solutions of $Ti(OC_2H_5)_4$ and either tantalum pentaethoxide, $Ta(OC_2H_5)_5$,* or niobium pentaethoxide, $Nb(OC_2H_5)_5$,* in 200-proof anhydrous ethanol. The hydrolysis reactions were conducted in a glove box under a dry N₂ atmosphere. In a typical experiment, a 0.2M solution of $Ti(OC_2H_5)_4$ containing the appropriate amount of the dopant alkoxide was hydrolyzed by an equal volume of 0.9 to 1.0M solution of deionized water in ethanol. The water solution was added to the alkoxide solution and stirred (the order of addition is reversible); after mixing, the solution concentrations of the alkoxide and water were half their initial concentrations. For reactions conducted at 25°C, precipitation of a white powder occurred in 20 to 60 s, where time increased as the concentration of either the alkoxide solution or the water solution was decreased. For synthesis of doped TiO₂ powders containing 0.5% (weight) of Nb₂O₅ or Ta₂O₅, ≈1 mL of ≈0.3M $Nb(OC_2H_5)_5$ or $Ta(OC_2H_5)_5$ stock solution in ethanol was mixed with ≈600 mL of the 0.2M $Ti(OC_2H_5)_4$ solution. To help ensure homogeneous nucleation of the doped TiO₂ particles, the 200-proof anhydrous ethanol was ultrafiltered through 0.22 μm pore-size filters.† Generally, however, this procedure was not performed with the other liquid reagents.

The singly-doped TiO₂ powder was then washed once with deionized water and ultrasonically redispersed in a dilute aqueous solution of $BaCl_2$, $CuCl_2$, or $SrCl_2$. An aqueous solution of $(NH_4)_2CO_3$ was added to the dispersion and stirred, leading to the precipitation of the respective metal carbonate (e.g. $BaCO_3$, $CuCO_3$, $SrCO_3$) onto the surface of the singly-doped TiO₂ powder. Typically, ≈10 mL of metal chloride solution of ≈0.01M concentration was added to a 750 mL dispersion of the singly-doped TiO₂ powder, followed by the addition of ≈7 to 10 mL of 0.05M $(NH_4)_2CO_3$ solution to precipitate the metal carbonate. These concentrations were appropriate for adding 0.1% (weight) of BaO, CuO, or SrO to a 9.3 g batch of TiO₂ powder.

If desired, other soluble salts such as nitrates may be used instead of chlorides to avoid Cl^- contamination in the powder. Also, other insoluble salts such as sulfates could be precipitated rather than carbonates. However, two major advantages of adding Ba^{2+}, Cu^{2+}, and Sr^{2+} as carbonates are the extremely low solubility products of the carbonates (and thus quantitative dopant precipitation) and the dissociation to the respective oxide and CO_2 gas on heating. Other salts with larger solubility products may not give quantitative doping and may leave undesirable anions (e.g. SO_4^{2-}) on decomposition.

The doubly-doped TiO₂ powder was centrifuged to remove the salt solution, redispersed in deionized water, and then centrifuged, redispersed, and centrifuged again before being dried at 80°C. Chemical and physical properties were measured by a variety of techniques. Some samples of pure TiO₂, singly-doped TiO₂, and doubly-doped TiO₂ were also dry-pressed at 31 MPa and then isostatically pressed at 276 MPa. The resulting pills were typically sintered at 1400°C for 1 h before electron probe microanalysis (EPMA).

Two other methods have also been used to prepare singly-doped TiO₂ powders. Strontium isopropoxide, $Sr(^iOC_3H_7)_2$, was used to make SrO-doped TiO₂ with 0.67% SrO. The $Ti(OC_2H_5)_4$ (≈0.19M) and $Sr(^iOC_3H_7)_2$ (≈5 × 10⁻⁴M) were mixed together in an ethanol solution which was then hydrolyzed by adding an H₂O solution (≈0.89M) in ethanol and stirring. Powder precipitation occurred in ≈30 s at 29°C. Scanning electron micrographs showed particles with an average diameter of ≈0.4 μm.

Singly-doped TiO₂ powder containing ≈0.5% Nb₂O₅ was made by hydrolyzing a mixture of $Ti(OC_2H_5)_4$ and $Nb(OC_2H_5)_5$ in ethanol in a packed bed crystallizer.[9] In essence, this continuous reaction system consisted of a glass tube packed with small glass beads (≈250 μm diameter). The alkoxide solution and water solution were pumped into the reactor where hydrolysis occurred, and a TiO₂ powder dispersion was collected at the reactor outlet. Several experiments were conducted on the synthesis of Nb₂O₅-doped TiO₂ in this system.

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Fig. 2. Scanning electron micrograph of SrO, Nb_2O_5-doped TiO_2 powder. This powder was not sedimented into a compact (bar=1 μm).
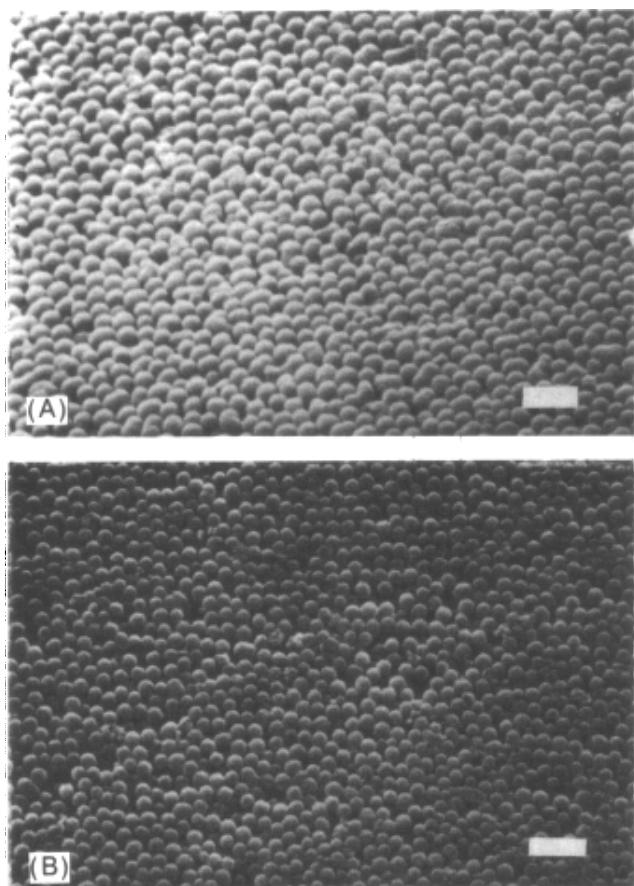
Fig. 1. Scanning electron micrographs of (A) top surface of pure TiO_2 compact and (B) top surface of BaO, Nb_2O_5-doped TiO_2 compact. Both compacts made by gravity sedimentation (bar=1 μm).

Results and Discussion

Figure 1 illustrates pure TiO_2 powder made by the controlled hydrolysis of $Ti(OC_2H_5)_4$ and BaO, Nb_2O_5-doped TiO_2 powder, and Fig. 2 shows an SrO, Nb_2O_5-doped TiO_2 powder. These figures, which are representative of the size, shape, and state of agglomeration of the various doped TiO_2 powders, illustrate several important points. First, the doped TiO_2 powders and the pure powders have a spheroidal shape; this is true of all doped TiO_2 compositions which have been prepared. Second, the doped TiO_2 powders are in the same size range as the pure TiO_2 powder, 0.3 to 0.7 μm in diameter. This size range is representative of the mean particle diameter in different batches of doped TiO_2 powders made at slightly different temperatures and with different reactant concentrations and is not the size distribution within a single batch of powder. The pure TiO_2 powder in Fig. 1 is $\approx$0.4 μm in diameter, the BaO, Nb_2O_5-doped TiO_2 powder is $\approx$0.3 μm in diameter, and the SrO, Nb_2O_5-doped TiO_2 powder is $\approx$0.6 μm in diameter. Third, the visually estimated particle size distribution from SEM micrographs is approximately the same for both the doped and pure TiO_2 powders (standard deviation $\approx$30% of the mean). Typically, the size-range distribution is very narrow with the size ratio of the largest particles to the smallest particles <2, and the ratio of the largest particles to the average particle is $\approx$1.5. Fourth, the doped TiO_2 powder exists predominantly as unagglomerated singlet particles. Again this desirable characteristic is also present in the pure TiO_2 powders.[1,10] Fifth, the micrographs show that only one particle population is present in the doped TiO_2 powder samples. The doping process gives TiO_2 particles containing the Nb_2O_5 or Ta_2O_5 dopants rather than TiO_2 particles mixed with a large number of smaller Ta_2O_5 or Nb_2O_5 particles. Furthermore, scanning electron microscopy X-ray maps (Sr, Nb, Ta) of singly-doped and doubly-doped TiO_2 powders show uniform dopant distributions that match the respective Ti X-ray maps. Thus, the dopants are not concentrated in large clumps but appear to be uniformly dispersed within the TiO_2 particles (in the case of Nb_2O_5 or Ta_2O_5) or uniformly covering the TiO_2 particles (in the case of BaO, CuO, or SrO).

Table I summarizes the measured physical properties for pure, singly-doped, and doubly-doped TiO_2 powders. X-ray diffraction showed t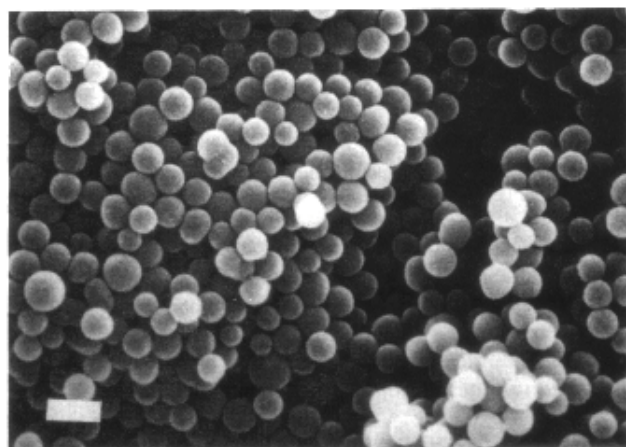hat all powders were amorphous. As mentioned previously, the pure and doped TiO_2 powders also have the same particle size range, shape, and structure. Density measurements using a stereo-pycnometer[‡] gave the same results for all three types of powder. Surface area measurements by a multipoint BET[§] method gave surface areas for powders washed with deionized water which are in the same range as surface areas of pure TiO_2 powders prepared by Barringer.[10] The high surface areas of the water-washed pure TiO_2 powders were attributed to a surface coating of fine spherical precipitates which resulted from the rapid hydrolysis of residual (unreacted) ethoxide on contact with water; presumably the same effect caused the high surface area observed for the singly-doped and doubly-doped TiO_2 powders.

Simultaneous differential thermal analysis-thermogravimetric (DTA-TG)[¶] studies were conducted on pure, singly-doped, and doubly-doped TiO_2 powders. Weight loss on heating to 1100°C ranged from 2% to 21%. The observed weight loss correlated with the treatment of the powder after synthesis. Powders which were not washed or previously heated above 80°C lost the most weight, 21%. Powders which had been washed and then calcined at 450°C for 30 min lost the least weight, 2% to 5%. Most of the weight loss is due to water loss at $\approx$120° to 170°C, the remainder results from burnoff of organics at $\approx$250° to 400°C. The DTA curve shows an endothermic peak in the temperature range where the water is lost and one or several exothermic peaks in the region where the organics are burned off and crystallization occurs. Several exotherms are observed for TiO_2 powders made from reactions where alkoxy group exchange can occur, e.g. $Ti(^iOC_3H_7)_4$ hydrolyzed in ethanol or $Ti(^nOC_4H_9)_4$ hydrolyzed in ethanol. The observed water losses of $\approx$10% by weight correspond to one-half H_2O molecule per TiO_2 molecule, which is assumed to be co-

Table I. Physical Properties of TiO_2 Powders

	Powder*		
	Pure	Singly doped	Doubly doped
Precursor(s)[†]	$Ti(OC_2H_5)_4$	$Ti(OC_2H_5)_4$, $M(OC_2H_5)_5$	$Ti(OC_2H_5)_4$, $M(OC_2H_5)_5$, $M'Cl_2$
Crystal form	Amorphous	Amorphous	Amorphous
Average particle size range (μm)	0.3–0.7	0.3–0.7	0.3–0.7
Density (g/cm^3)	3.0–3.2	3.0–3.2	3.0–3.2
Surface area (m^2/g)	170–200	200–250	100–300
Shape	Spheroidal	Spheroidal	Spheroidal
Structure	Unagglom-erated	Unagglom-erated	Unagglom-erated

*All samples washed with water. [†]M=Nb, Ta; M'=Ba, Cu, Sr.

Table II. Dopant Levels* and Impurities in Doped TiO_2 Powders

	Amount detected in powder (wt%)			
Oxide	TiO_2	TiO_2+ 0.1% Ta_2O_5	TiO_2+ 1% Nb_2O_5	$TiO_2+1\%$ BaO+ 1% Ta_2O_5
BaO	<0.01	<0.01	<0.01	1.02
SrO	<0.01	<0.01	<0.01	<0.01
Nb_2O_5	<0.01	<0.01	0.98	<0.01
Ta_2O_5	0.03	0.11	<0.01	1.01

*Data from inductively coupled plasma emission spectroscopy.

Table III. Processing Effects on Doped TiO_2 Chemistry

		Amount present (wt%)	
Sample No.	Oxide	Powder	Ceramic
1	Nb_2O_5	0.22±0.007	0.23±0.03
	SrO	0.29±0.009	0.33±0.07
2	Nb_2O_5	0.72±0.02	0.73±0.06
	SrO	0.25±0.008	0.28±0.15
3	Nb_2O_5	0.77±0.02	0.78±0.04
	CuO	0.26±0.008	0.25±0.03

Table IV. Representative Impurity Levels in Doped TiO_2 Powders as Determined by Inductively Coupled Plasma Emission Spectroscopy

Element	Amount (ppm)	Element	Amount (ppm)
Al	<30	La	<20
B	<20	Mg	<10
Ba	<20	Mn	<10
Ca	≈50	Mo	≤20
Cd	<10	Na	<50
Co	<50	Ni	<30
Cr	<30	Si	0.01–0.1%*
Cu	<50	Ta	<100
Fe	<50	V	<20
Gd	<50	Zr	≈100

*See text.

ordinately bonded to the Ti ions in the "open," amorphous structure.

Extensive chemical analyses have been performed on samples of doped TiO_2 powders and sintered ceramics. The results of these analyses, which are described below, demonstrate that the alkoxide doping methods give good control over the desired chemistry with a low level of contaminants. Most of the analytical data is from inductively coupled plasma emission spectroscopy (ICP); however, confirming data have been obtained by other techniques including instrumental neutron activation analysis (INAA), direct coupled plasma emission spectroscopy (DCP), and EPMA.** Table II gives the analyses for four of the dopants in four samples of ethoxide-derived TiO_2 powders. One sample is pure TiO_2, two are singly-doped TiO_2 samples, and one is doubly-doped TiO_2. These results show that the alkoxide hydrolysis and carbonate precipitation methods give doped TiO_2 powders of the desired dopant composition in the 0.1% to 1.0% weight range.

The reproducibility of the doping methods is illustrated by two representative examples. The ICP analyses of two different samples of TiO_2 powder doped with ≈0.4% CuO and ≈0.6% Nb_2O_5 gave Ti/Cu weight ratios of 181 and 183 and Ti/Nb weight ratios of 147 and 144. The ICP analyses for the two dopants show very good agreement, thus demonstrating the reproducibility of the doping methods. In a second comparison, Ti/Nb weight ratios for two different TiO_2 powders doped with ≈0.5% Nb_2O_5 were 178 and 173. Sample 1 was doped by the alkoxide hydrolysis process in the glove box, whereas sample 2 was doped by the same process in the plug-flow reactor. Again, the very good agreement between the dopant levels in the two samples shows the reproducibility of this technique. Furthermore, these data show that the doping process is applicable to a continuous reactor system, which has the potential for producing large quan-

tities of material with precisely controlled composition.

The ICP, DCP, and EPMA analyses have also been used to study the effects of subsequent processing on the chemistry of the doped TiO_2 samples; Table III gives analytical results for doped TiO_2 powders and sintered ceramics. The powders were analyzed by DCP and the ceramics were analyzed by EPMA. These data show that the processing steps after powder synthesis do not change the chemistry of the powders doped with Nb_2O_5, SrO, and CuO. Confirming results have also been obtained from ICP analyses of doped TiO_2 powders and ceramics.

The ICP method and semiquantitative mass spectrometry have also been used to study impurities present in the doped and pure TiO_2 powders, respectively. Table IV lists representative impurity levels for doped TiO_2 powders; these data were derived from 56 ICP analyses of 24 samples. Although ICP analyses of pure TiO_2 indicated cation impurities in the <10 to 50 ppm (weight) range, semiquantitative mass spectrometry showed no presence of many of these impurities, whereas others such as Al, Ca, Fe, and Mg were present at levels ≤10 ppm.[1,10] The detection limits of ICP analysis for the various cation im-

purities vary as a function of sample size and composition and thus may be much higher than the actual level present (e.g. the Gd <50 ppm detection limit is probably higher than the actual Gd content of the samples, but interference effects from other elements and small sample size result in a higher detection limit). Levels of other impurities also vary because of impurities present in the various reagents used in the doping process. For example, SrO-doped TiO_2 made by the hydrolysis of $Ti(OC_2H_5)_4$ and $Sr(^iOC_3H_7)_2$ contained 41 ppm Ba and 92 ppm Ca; these two alkaline earths were probably impurities present in the $Sr(^iOC_3H_7)_2$ reagent. Much lower Ba impurity levels (typically <20 ppm) were found in Ta_2O_5- and Nb_2O_5-doped TiO_2 powders. The alkaline earth Ba was probably not present as an impurity in alkoxides of the chemically dissimilar (group V elements) Nb and Ta.

Analysis of all the ICP and EPMA results for pure and doped TiO_2 powders and ceramics leads to the conclusion that most of the impurities present in the samples result from impurities already present in the reagents and not impurities introduced during synthesis and subsequent processing. The exception is Si, which is present in high (0.01% to 0.1%) and

variable concentrations in many samples. The preliminary results indicate that Si at ≈100 ppm may be introduced from the bottles within which the alkoxides are contained and the glassware used for the reactions. Higher Si concentrations (≈0.1%) in sintered ceramics may result from SiO volatilized from mullite furnace tubes. Although further work to define impurity sources and levels is desirable, present results indicate that proper purification of the reagents will lead to reductions in levels of several impurities, e.g. Ca and Zr, and changes in reaction vessels and sintering procedures may lead to reductions in the Si content.

CONCLUSIONS

This study has demonstrated that doped TiO_2 powders composed of approximately monosized, spheroidal, unagglomerated particles can be prepared by the controlled hydrolysis of metal alkoxides

and precipitation of inorganic salts. The size, shape, and state of agglomeration of the doped TiO_2 powders are similar to those of pure TiO_2 powders made by the hydrolysis of titanium alkoxides.[1] Powders having a variety of chemical compositions can be reproducibly synthesized while maintaining generally low cation impurity levels.

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