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Synthesis of Uniform Titanium and 1:1 Strontium-Titanium Carboxyhydrosols by Controlled Hydrolysis of **Alkoxymetal Carboxylate Precursors**

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Uniform inorganic carboxyhydrosols containing titanium or strontium and titanium cations were precipitated from isopropyl alcohol solutions by the controlled hydrolysis of metal alkoxycarboxylate precursors. The hydrolysis of various triisopropoxytitanium carboxylate compounds yielded the capability to control particle size. Spherical particles of carboxyhydrosols were prepared in mean sizes from 0.4 to 2.9 μ m. Controlled hydrolysis of quintaisopropoxystrontium titanium octanoate resulted in slightly agglomerated, uniform 1-µm spheres in a solvent medium in which controlled precipitation of uniform powders was not previously possible. Conversion of the hydrous oxide carboxylate precipitate to the oxide via calcination or hydrothermal treatment was possible. [Key words: titanium, strontium, organometallic, powders, processing.]

I. Introduction

THE utilization of colloidal uniform spheres satisfies a spectrum of needs in both scientific and technological areas. Uniform latex particles are used for pigments, the calibration of electron microscopes, precipitation and colloid science, and various medical diagnostic tests. In many cases, the particles contain functional groups that serve a variety of purposes, such as antigen or antibody binding.1 Uniform ceramic hydrous oxides have exhibited utility in the study of corrosion, catalysis, pigments,² and the preparation of defect-free high-technology ceramics.34

To date, the preparation or application of uniform ceramic spheres containing specific functionalities has not been discussed. This paper presents simple methods for preparing powders that incorporate organocarboxylate functionalities for both one- and two-component hydrous oxides and that can alternatively be decomposed to form a reactive ceramic oxide.

The hydrolysis of metal alkoxycarboxylates was selected to achieve the above objectives. These compounds react with water in the following manner:

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$$M(OR)_x OOCR + H_2O = RCOOM(OR)_{x-1} - OH + ROH$$
(1)

The alkoxide group is unstable, but the carboxylate is stable against hydrolysis.⁵ This hydroxyl can condense in one of the following ways:

$$RCOOM(OR)_{x-1} - OH + HO - M(OR)_{x-1}OOCR$$

= RCOOM(OR)_{x-1} - O - M(OR)_{x-1}OOCR + HOH (2)

 $RCOOM(OR)_{x-1}$ -OH + RO-M(OR)_{x-1}OOCR

$$= \text{RCOOM}(\text{OR})_{r-1} - O - M(\text{OR})_{r-1} OOCR + \text{ROH}$$
(3)

The above hydrolysis and condensation process produces polymers in solution which can supersaturate a solution and precipitate via nucleation and growth processes. These hydrolysis and polymerization processes must be controlled to prepare uniform powders. This work shows how this can be easily facilitated using concentration, temperature, and chemical moieties as critical processing variables.

II. Experimental Procedure

Unless otherwise noted, all reagents were purified using distillation procedures to remove undesired impurities. Isopropyl alcohol and triethylamine were distilled over calcium hydride. The carboxylic acids were distilled over P2O5. Deionized hydrolysis water ($\approx 18 \text{ M}\Omega$) was prepared using ion-exchange resins.[‡] The water was degassed free of CO₂ by bubbling N₂ gas through the liquid. All reactions were conducted under a N2 atmosphere using standard procedures for handling air-sensitive materials.

Alkoxymetal carboxylates, the compounds to be hydrolyzed, were synthesized by the replacement of alkoxide groups in one of the following manners. Triisopropoxytitanium propanoate, (i-PrO)₃TiOOCC₂H₅, was prepared by adding 1 equiv of propanoic acid[§] dropwise to titanium tetraisopropoxide[¶] under N₂.

$$Ti(O-i-Pr)_4 + C_2H_5COOH \longrightarrow$$

$$(i-PrO)_{3}TiOOCC_{2}H_{5} + i-PrOH$$
 (4)

Diisopropoxytitanium dioleate was synthesized in a similar manner. In general, all of the alkoxycarboxylate syntheses required careful addition of the acid to the reaction medium because the exothermic nature of this reaction can raise the temperature of the reaction medium and generate reaction products (e.g., $(RCOO)_2Ti = O$ and RCOO-i-Pr) which give undesirable hydrolytic properties.^{6,7}

The following synthesis routes were employed to prepare quintaisopropoxystrontium titanium octanoate, (i-PrO)₅SrTiOOC-n- C_7H_{15} :

$$Sr + 2i$$
-PrOH \longrightarrow $Sr(O-i$ -Pr)₂ + H₂ (5)

^{*}Millipore, Bedford, MA. [§]Eastman Kodak, Rochester, NY.

¹Alfa Products, Darvers, MA. **Model EM201, Philips Electronic Instruments, Eindhoven, the Netherlands. ¹¹Model S-530, Hitachi, Danbury, CT. ¹²Model STA 429/3/6, Netsch, Exton, PA. ⁵⁹Ratio recording spectrometer, Perkin-Elmer Corp., Norwalk, CT. ⁵⁹Spectra-Tech, Stamford, CT.

$$Ti(O-i-Pr)_{4} + n - C_{7}H_{15}COOH \longrightarrow$$

$$(i-PrO)_{3}TiOOC - n - C_{7}H_{15} + i-PrOH \qquad (6)$$

$$(i-PrO)_{3}TiOOC - n - C_{7}H_{15} + Sr(O-i-PrO)_{2} \longrightarrow$$

$$-PrO)_{3}TiOOC-n-C_{7}H_{15} + Sr(O-i-PrO)_{2} \longrightarrow$$

$$SrTiOOC-n-C_7H_{15}(i-PrO)SrTiOOC-n-C_7H_{15}$$
(7)

Method 2

$$Sr(O-i-PrO)_2 + Ti(O-i-Pr)_4 \longrightarrow SrTi(i-PrO)_6$$
 (8)

 $SrTi(i-PrO)_6 + n-C_7H_{15}COOH \longrightarrow$

SrTiOOC-
$$n$$
- $C_7H_{15}(i$ -PrO)SrTiOOC- n - C_7H_{15} + i -PrOH

(9)

Strontium diisopropoxide-in-isopropyl alcohol solutions were used for methods 1 and 2. Solutions ranging in concentration from 1 to 2 m were synthesized using the method of Smith et al.⁸ Reagent-grade Sr metal (99% pure)[¶] was used as received and commercial octanoic acid[§] was obtained. To ensure the preparation of 1:1 strontium: titanium molar ratio solutions, the strontium alkoxide solution was gravimetrically assayed as SrSO₄ and titanium tetraisopropoxide was gravimetrically assayed as rutile using classical methods.9,10

Dropwise addition of all reagents at room temperature was critical for obtaining a solution free of the byproducts described above and insoluble alkoxymetal carboxylate precipitates. In all cases precipitates were observed, but given sufficient time a clear solution was obtained. However, attempts to substitute more than one alkoxide group with an octanoate group or to prepare other monosubstituted carboxylate precursors, such as oleate and propanoate, failed to produce solutions free of precipitate.

In all of the syntheses described above, no attempt was made to remove the isopropyl acohol product since all of the precursors were later diluted in isopropyl alcohol as the precipitating medium. After preparation, all precursor solutions were stored under N₂ in a glove box.

Most hydrolyses were conducted at room temperature by the rapid addition of a water-in-isopropyl alcohol solution in an equivolume portion to a stirred isopropyl alcohol solution of the alkoxymetal carboxylate. The various precursors employed and their concentrations are summarized in Table I. Hydrolysis reactions conducted at -78°C were performed in dry ice/isopropyl alcohol baths. After this initial mixing period, the solutions were allowed to stand undisturbed. Induction times were recorded and ranged from less than a minute to a few hours.

The particle size, particle-size distribution, and degree of agglomeration of the hydrolysis products were semiquantitatively assessed using transmission** and scanning^{††} electron microscopy. Thermal gravimetric analysis,^{‡‡} transmission infrared spectroscopy, and powder X-ray diffraction were used to characterize the powder chemistry. Powders were suspended in Nujol^{TM,¶} or Fluorolube^{TM,¶} and smeared on KCl windows.

III. Results and Discussion

(1) Isopropoxytitanium Carboxylate

Controlled hydrolysis reactions were first conducted using tri-

1	Fable I.	Hvdrolvsis Conditions	s for the Preparation of	Titanium and Strontium	Titanium Hydrous Oxide Carboxyla	ites
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Sample	Precursor	Precursor concentration (mol/L)	H ₂ O: precursor	Temperature (°C)
TAP-1	(<i>i</i> -PrO) ₃ TiOOCC ₂ H ₅	0.075	12:1	25
TAP-2	$(i-PrO)_3T_1OOCC_2H_5$	0.075	30:1	25
TAP-3	$(i-PrO)_3TiOOCC_2H_5$	0.075	50:1	25
TAO-1	$(i-PrO)_2TiOOC(01)_2*$	0.012	83:1	25
TAO-2	$(i-PrO)_2TiOOC(01)_2*$	0.012	167:1	25
STAO-1	$(i-PrO)_5$ SrTiOOC- $n-C_7H_{15}$	0.0039	10:1	25
STAO-2	$(i-PrO)_5$ SrTiOOC- $n-C_7$ H ₁₅	0.0098	5:1	25
STAO-3	$(i-PrO)_5$ SrTiOOC- $n-C_7H_{15}$	0.0098	$8:1^{\dagger}$	25
STAO-4	$(i-PrO)_5$ SrTiOOC- $n-C_7H_{15}$	0.079	3:1	25
STA-1	SrTi(O-i-Pr) ₆	0.11	9:1	-78

*01 is CH₂(CH₂)₂CH=CH(CH₂)₂-, [†]Hydrolysis solution contained 0.0098M triethylamine.

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Fig. 1. Scanning electron micrographs of monodisperse titanium hydrous oxide propanoates obtained as described in Table I: (A) sample TAP-1, (B) sample TAP-2, and (C) sample TAP-3.

isopropoxytitanium *n*-propanoate (Table I). Nucleation induction times ranged from 2 min to several hours as the water:precursor molar ratio was varied from 12:1 to 50:1. In contrast, with comparable reactant concentrations, induction times for particle nucleation in the hydrolysis reactions of $Ti(OEt)_4$ were less than 2 min.^{11,12} As with $Ti(OEt)_4$ hydrolysis, monodisperse powder was obtained (Fig. 1).

The variation in particle size of powders obtained from triisopropoxytitanium *n*-propanoate hydrolysis differed slightly from that obtained from Ti(OEt)₄ hydrolysis. As with Ti(OEt)₄-derived powders,^{11,12} the particle size of triisopropoxytitanium *n*-propanoatederived powders increased as water concentration decreased (Table II). However, the mean particle size obtained from each of the two precursors differed significantly. Other researchers report that, despite the range of Ti(OEt)₄ concentration (0.075*M* to 0.2*M*) and H₂O:precursor ratios (3:1 to 3:13) examined, only particle sizes smaller than 0.6 μ m could be obtained via solution hydrolyses.¹¹ In contrast, we found that triisopropoxytitanium *n*-propanoate hydrolysis resulted in a powder that crossed the submicrometer-micrometer size range (0.4 to 1.2 μ m).

Although water played a critical role in controlling the particle size, it also controlled the degree of agglomeration. Figure 1 shows how increasing the H_2O : precursor ratio increased the degree of agglomeration. Faster hydrolysis kinetics resulted as the H_2O : precursor ratio increased, resulting in higher particle densities. Higher particle densities during nucleation and growth of the powder resulted in faster agglomeration kinetics. The use of an in situ sterically stabilizing surfactant, such as that reported by Jean and Ring, ¹³ would reduce agglomeration and allow synthesis of an agglomerate-free submicrometer powder.

The effect of increasing the carboxylate chain length was investigated using dialkoxytitanium dioleate. Since this compound is not very soluble in isopropyl alcohol, it was dissolved in ethyl alcohol by refluxing for ≈ 2 h. Hydrolysis of 0.012M diisopropoxytitanium dioleate at room temperature formed the powders shown in Fig. 2. Increasing the water concentration by a factor of 2 decreased the particle size by nearly a factor of 3 (2.9 to 1.2 μ m). This is a considerably larger particle size than that obtained via Ti(OEt)₄ hydrolysis. The indentations on the particles prepared at a H₂O: precursor molar ratio of 167:1 are believed to be fracture indentations due to the separation of aggregates. This is believed to have occurred during the particle rinsing process, where ultrasonic forces were used to re-suspend powder cakes comprised of weakly bonded aggregates.

5 µm

Experimental evidence suggests that only a small fraction of the carboxylate groups were hydrolyzed during precipitation, and the oleate group could be found in the powder. First, quantitative estimation of the propanoic acid content in the supernatant of the precipitation medium using titrimetric and infrared spectroscopic methods revealed that, at the most, 18 wt% of the theoretical yield of acid was present. This degree of hydrolytic resistance is consistent with hydrolysis studies conducted with zirconium carboxylates.⁵ Second, thermal gravimetric analysis showed that the weight loss of precipitate prepared from the triisopropoxytitanium

 Table II.
 Effect of the Water: Precursor

 Ratio on Particle Size

Sample	Precursor concentration (mol/L)	H ₂ O: precursor	Induction time	Particle size (µm)
TAP-1 TAP-2 TAP-3 TAO-1 TAO-2	0.075 0.075 0.075 0.012 0.012	12:1 30:1 50:1 83:1 167:1	Several hours 20 min 2 min	1.2 0.9 0.4 2.9 1.2



Fig. 2. Scanning electron micrographs of monodisperse titanium hydrous oxide propanoate obtained as described in Table I: (A) sample TAO-1 and (B) sample TAO-2.

propanoate was on the order of 38.7 wt%. This is significantly greater than what would be expected for titanium hydrous oxide, which for a worst case has a weight loss of 20 wt%, but is slightly less than what would be expected for TiO_{1.5}(OOCC₂H₃), which has a weight loss of \approx 45 wt%. Third, Fig. 3 shows that when the precipitate (sample TAP-1) was calcined at 500°C for 2 h to the oxide, the resulting compound showed little of the initial physical characteristics found in the powder. The degree of degradation is evidence of a large amount of volatile matter that must have left in an explosive manner.

The calcination results also indicate that hydrothermal rather than calcination routes should be sought if a uniform, spherical, disperse titanium dioxide is desired. Such results have been obtained using uniform alkoxide-derived titanium hydrous oxide to obtain spherical polycrystalline anatase powders.¹⁴

(2) Quintaisopropoxystrontium Titanium Octanoate

In comparison with the titanium metal-organic systems discussed above or strontium titanium hexaisopropoxide, the hydrolytic and resultant precipitation behaviors of quintaisopropoxystrontium titanium octanoate solutions contrast sharply. First, the strontium titanium metal-organic systems react significantly more rapidly than the titanium metal-organic systems. This is reflected by the lower reactant concentrations required for controlled hydrolysis of the strontium titanium metal-organic systems as compared with the titanium metal-organic systems (Table I). Second, controlled hydrolysis of solutions over a range of concentrations and temperatures, regardless of the choice of alkoxide group or presence of an organic base, does not aid in obtaining spherical, disperse,



Fig. 3. Scanning electron micrograph of the precipitate formed after calcining sample TAP-1. Note that this precipitate has only a portion of the initial physical characteristics found in the titanium hydrous oxide propanoate.

submicrometer powder (e.g., sample STA-1).¹⁵ Instead, an ultrafine hydrous oxide forms that is difficult to process. A powder representative of the conditions stated above is shown in Fig. 4(A); the specific reaction conditions are stated in Table I.

On the other hand, controlled hydrolysis of the quintaisopropoxystrontium titanium octanoate solutions having induction times of a few seconds to 20 min produced a more desirable, $\approx 1-\mu m$ spherical powder (Fig. 4(B)). Thus, replacement of an alkoxide group with a carboxylate group is a critical processing variable for controlling the physical powder characteristics. However, future work is needed to further minimize the degree of aggregation, because concentration, addition of an organic base (sample STAO-3), and stirring variables do not appear to control this characteristic.

The carboxylate group appears to have a role in controlling the solubility of hydrolysis polymers formed during the hydrolysis reaction. This is illustrated in Table II. At identical water: alkoxide ratios, carboxylate-substituted precursors (method 2) precipitated powder, whereas a double alkoxide solution at twice the precursor concentration did not. Hydrolysis solutions containing $n-C_7H_{15}COOH$ mixed with a double alkoxide ratio was 1:1 or greater. The decrease in solubility of the hydrolysis polymers produced from quintaisopropoxystrontium titanium octanoate is attributed to the presence of a hydrolysis-resistant polar carboxylate group. This contrasts with the hydroxyls and alkoxide solution. The difference in solubility behavior is believed to control the nucleation and growth processes that ultimately control particle size.

Experimental evidence suggests the presence of octanoate groups in the hydrolysis product. Infrared characterization (Table III) of the powder prepared from the method 1 precursors exhibits evidence of hydroxyl (O-H), hydrocarbon (C-H), and carboxylate (COO⁻) groups (Table IV), which indicates that ionic octanoate groups were present.¹⁶⁻¹⁸ In addition, the powder did not wet water, indicating its hydrophobic nature due to the presence of octanoate groups. Finally, the hydrolysis product of precursors prepared from either method 1 or method 2 was amorphous and calcined to form SrTiO₃ with a loss on ignition of ≈ 47 wt% in air at 1050°C. This weight loss corresponds well to an empirical formula, SrTiO_(2.0-x/2)(OH)_(1+x)OOC-*n*-C₇H₁₅, (where 0 < x < 2); this compound has a weight loss ranging from 44 to 47 wt%.

In the interest of obtaining an oxide while maintaining a spherical powder morphology, hydrothermal processing was utilized instead of a calcination approach. Under various hydrolysis conditions, crystalline SrTiO₃ powder can be obtained directly by refluxing alkoxide solutions or dispersions of amorphous precipitate at atmospheric pressure.^{8,15} However, hydrolysis of the quintaisopropoxystrontium titanium octanoate or dispersions of the amorphous hydrolysis product under similar conditions did not



Fig. 4. Transmission electron micrographs showing the contrasting powder characteristics obtained for controlled hydrolysis of (A) strontium titanium hexaisopropoxide (sample STA-1) and (B) quintaisopropoxystrontium titanium octanoate (sample STAO-2).

Table III. Effect of Carboxylate Substitution on the Solubility of Hydrolysis Products

Precursor solution	Precursor concentration (mol/L)	H ₂ O: precursor	Acid: precursor	Precipitation observed	Induction time (s)
SrTi(OPr-i),OOCR*	0.020	3:1		Yes	300
SrTi(OPr- i) $_{6}^{\dagger}$	0.039	3:1		No	
$SrTi(OPr-i)_{6}$	0.020	8:1		No	
$SrTi(OPr-i)_{6}$	0.020	8:1	1:4	No	
SrTi(OPr)6	0.020	8:1	1:2	No	
SrTi(OPr) ₆	0.020	8:1	1:1	Yes	20
$SrTi(OPr-i)_6$	0.0125	8:1	2:1	Yes	120

*R is *n*-C₇H₁₅; method 2 precursor. *Strontium titanium hexaisopropoxide.

Table IV.Infrared Spectra of QuintaisopropoxystrontiumTitanium Octanoate Hydrolysis Product Derived from the
Method 1 Precursor

Absorption band (cm ⁻¹)*	Peak assignment	
3400 (br)	O-H stretch	
2960 (s)	C-H stretch	
2930 (s)	C–H stretch	
2860 (s)	C-H stretch	
1550 (s)	Symmetric COO ⁻ stretch	
1410 (s)	Asymmetric COO ⁻ stretch	

*br is broad; s is strong.

lead to formation of a crystalline oxide. This behavior has been attributed to the hydrolytic resistance of the octanoate group. In order to force the hydrolysis, the room-temperature hydrolysis product of a method 2 precursor was autoclaved at 300° to 350° C in water for 12 h. The resulting SrTiO₃ crystallization produced polycrystalline spherical powder (Fig. 5) similar to that observed by Oguri *et al*.¹⁴

IV. Conclusions

The hydrolysis of various triisopropoxytitanium carboxylate compounds yielded the capability to control particle size. Spherical particles of carboxyhydrosols were prepared ranging in mean size from 0.4 to 2.9 μ m. Controlled hydrolysis of quintaisopropoxystrontium titanium octanoate resulted in slightly agglomerated $\approx 1-\mu$ m spheres in a solvent medium in which controlled precipitation of uniform powders was not previously possible. Calcination or hydrothermal treatments are both viable routes for the conversion of the titanium hydrous oxide carboxylate or strontium titanium hydrous oxide carboxylate precipitate to the oxide. However, in the interest of processing with dispersed, narrow-size-distribution, spherical particles, hydrothermal processing allows better control of the physical characteristics during conversion to the oxide.



Fig. 5. Transmission electron micrograph of the spherical polycrystalline SrTiO₃ resulting from hydrothermal treatment of strontium titanium hydrous oxide octanoate.

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Structural and Thermodynamic Variation in Nickel Aluminate Spinel

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New structural and calorimetric data for samples of NiAl₂O₄ quenched from 600° to 1560°C are presented. The spinel remains stoichiometric for all heat treatments. Based on the refinement of X-ray powder patterns, it is shown that the degree of disorder, defined as the mole fraction of tetrahedral sites occupied by Al^{3+} , changes from x = 0.82 at 600°C to 0.78 at 1560°C. Simultaneously, the lattice parameter and enthalpy vary in a complex manner with quench temperature. The largest lattice parameter $(0.80500 \pm 0.00004 \text{ nm})$ and most exothermic enthalpy of annealing (heat released when sample is equilibrated at 780°C; -10.1 kJ/mol) occur for the sample quenched from 1100°C. A linear correlation exists between the heat of annealing and the lattice parameter. The results have been interpreted as a superposition of at least two effects: (1) the disordering of Ni²⁺ and Al³⁺ ions between octahedral (16d) and tetrahedral (8a) sites and (2) a second process, which may be a small amount of the disordering of ions into the usually empty (16c) sites. [Key words: aluminates, nickel, spinels, thermodynamics, heat treatment.]

I. Introduction

XIDE spinels have been investigated intensively in the solid-Ostate sciences for several decades because of usefulness as magnetic materials, semiconductors, pigments, catalysts, refractories, and as convenient model compounds to explore the relative stabilities of ions in octahedral and tetrahedral coordination. As common accessory minerals, petrogenetic indicators, and ores, they are ubiquitous geologic materials. Despite their deceptively simple structure, many spinels exhibit complex disordering phenomena involving the two cation sites. These processes have important consequences for both their thermochemical and physical properties.

A general formula for 2-3 oxide spinels is AB_2O_4 , where A and B are divalent and trivalent cations, respectively. The unit cell containing 8 formula units has the cubic space group Fd3m. The oxygen ions occupy 32e general positions and are arranged in an almost cubic closed-packed structure. Such an arrangement of ions leaves 64 tetrahedral and 32 octahedral interstices as possible sites for cations, of which only 8 tetrahedral (8a) and 16 octahedral [16d] sites are occupied. The completely normal spinel is one in which the divalent A cations occupy the 8 tetrahedral sites and trivalent B cations occupy the 16 octahedral sites (A)-[B₂]O₄. In the inverse spinel, (B)[AB]O₄, all 8 divalent A cations together with 8 trivalent cations occupy 16 octahedral positions and the remaining B cations occupy 8 tetrahedral positions. All distributions falling between these two extremes may also be realized, and it is convenient to define an additional parameter x, the degree of disorder, which is the fraction of tetrahedral sites occupied by B ions. So, a completely normal spinel has x = 0, a perfectly inverse one has x = 1, and a spinel with degree of inversion x has the formula $(A_{1-x}B_x)[A_xB_{2-x}]O_4$. Of special note is the completely "random" or "statistical" distribution with $(A_{1/3}B_{2/3})[A_{2/3}B_{4/3}]O_4$. Experimental studies show that many spinels approach the random distribution (x = 2/3) at high temperatures.

A number of the observed cation distributions in spinels can be explained by crystal field theory.^{1,2} However, in about one-third of the cases where this model is applicable, it does not predict the observed cation distribution correctly. Glidewell³ has shown that in many cases the change in the electrostatic part of the lattice energy with disordering is of much greater magnitude than any crystal field effects. Glidewell has improved the prediction of structure type by including both electrostatic and crystal field factors in calculation of the site stabilization energy. Burdett et al.⁴

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